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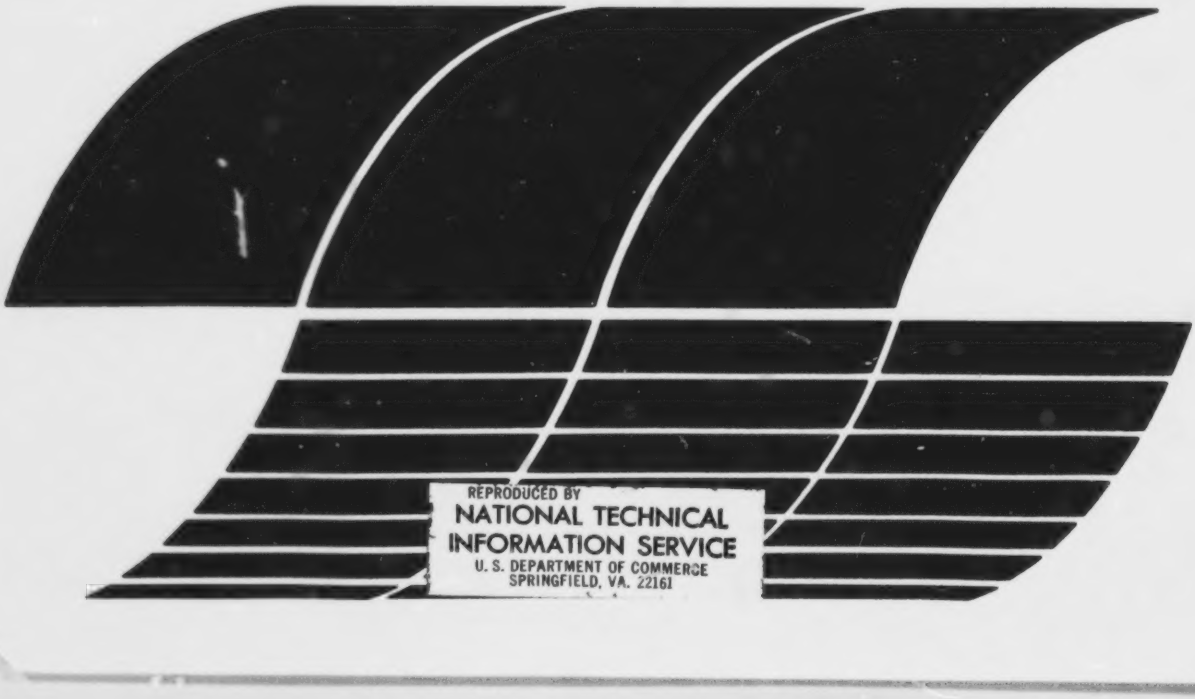

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16. ABSTRACT

The report gives results of an experimental investigation of coal pyrolysis and oxidation, and char oxidation to determine the effects of temperature and fuel/oxygen equivalence ratio on the conversion of coal-nitrogen to NOx. Experiments involved a laboratory laminar flow furnace under conditions representing pulverized coal combustors; i.e., heating rates of 1000 to 1 million K/sec, temperatures of 1000 to 2100 K, and residence times of 2 to 1000 milliseconds. The devolatilization experiments showed that no nitrogen loss occurred until 10 to 15% of the coal had been devolatilized, consistent with the hypothesis that coal-nitrogen is contained mostly in heterocyclic rings. Nitrogen was completely removed from the char by prolonged heating at above 1750 K, implying that nitrogen does not form condensed stable structures at pulverized flame temperatures, as does carbon. After initial fracture, loss of nitrogen and total weight loss are linearly correlated with a nitrogen-to-carbon slope of 1.25 to 1.5. Volatile nitrogen compounds accounted for the major fraction of NOx produced from coal-nitrogen, especially at high temperatures and low fuel/oxygen equivalence ratios. The results suggest that low NOx emissions from pulverized coal combustion are favored by a two-stage design: the first stage operated fuel-rich at high temperature; the second, fuel-lean at low temperature.

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Combustion Research on the Fate of Fuel-nitrogen under Conditions of Pulverized Coal Combustion

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ABSTRACT

An experimental investigation of coal pyrolysis and oxidation and char oxidation was performed with the objective of determining the effects of temperature and fuel/oxygen equivalence ratio on the conversion of coal-nitrogen to NO_x. Experiments were carried out in a laboratory laminar flow furnace under conditions representative of pulverized coal combustors, i.e., heating rates of $10^4 - 10^6$ °K/sec., temperatures of 1000 - 2100°K, and residence times of 2 - 1000 milliseconds.

Data on the devolatilization of coal were obtained at temperatures up to 2100°K, both as a function of time and under conditions of asymptotic yield. The devolatilization experiments showed that no nitrogen loss occurred until 10 - 15% of the coal had been devolatilized, consistent with the hypothesis that coal-nitrogen is contained mostly in heterocyclic rings. Nitrogen could be completely removed from the char by prolonged heating at temperatures above 1750°K, implying that nitrogen does not form condensed stable structures at pulverized flame temperatures as does carbon. After initial fracture, loss of nitrogen and total weight loss are linearly correlated with a nitrogen to carbon slope of 1.25 to 1.5. The pseudo-first order rate constant for initial nitrogen loss was found to be:

$$k = 9.3 \times 10^3 \exp\left[-22{,}700/RT\right]$$

Data on the conversion of coal-nitrogen to NO_x, under oxidative conditions, were obtained at temperatures up to 1750°K, for residence times up to one second. The conversion of coal-nitrogen to NO_x decreased monotonically with increasing fuel/oxygen equivalence ratio, and decreased slightly with increasing temperature. Oxidation experiments were also carried out on char in order to separate the individual contributions to NO_x emissions of volatile and char-bound nitrogen. The char used was prepared by the pyrolysis of coal at temperatures and residence times corresponding to those of the oxidation experiments. The conversion to NO_x of char-nitrogen was lower than the corresponding value for coal-nitrogen, while following trends similar to that of coal-nitrogen. It was found that volatile nitrogen compounds accounted for the major fraction of NO_x produced from coal-nitrogen, especially at high temperatures and low fuel/oxygen equivalence ratios. The results suggest that low NO_x emissions from pulverized coal combustors are favored by a two stage design, the first stage operated fuel-rich at high temperature, the second stage operated fuel-lean at low temperature.

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SECTION I

INTRODUCTION

Coal constitutes one of the major United States fossil fuel reserves. Exploitation of these reserves is, however, complicated by a number of problems, including their high nitrogen content which can contribute significantly to the emissions of nitrogen oxides (NO_x).

United States coals have nitrogen contents that average 1.4% nitrogen by weight. Typically, 20 to 60 percent of the nitrogen in a fuel is converted to nitrogen oxides in practical combustion devices. Higher conversions are obtained when the nitrogen content of the fuel is low or when the combustor is operated lean. At current levels of coal consumption of over 500×10^6 tons/year, a conversion efficiency of fuel-nitrogen to NO_x of 20% (assuming an average of 1.4% fuel-nitrogen in coal) would yield emissions exceeding 4.6×10^6 tons/year of NO_x (evaluated as NO_2). This is significant when compared with current estimates (Department of Transportation, 1976) of 10.3×10^6 tons/year emitted from stationary sources and 11.6×10^6 tons/year emitted from mobile sources.

The anticipated increase in utilization of fuels derived from coal provides the motivation for developing combustion processes that will yield low NO_x levels when fired with fuels having a high nitrogen content. This report presents the results of a study conducted at M.I.T. aimed at elucidating the mechanism of fuel-nitrogen conversion to NO_x in pulverized coal flames with the specific goal of developing a strategy for minimization of NO_x emissions through careful control and optimization of combustion conditions.

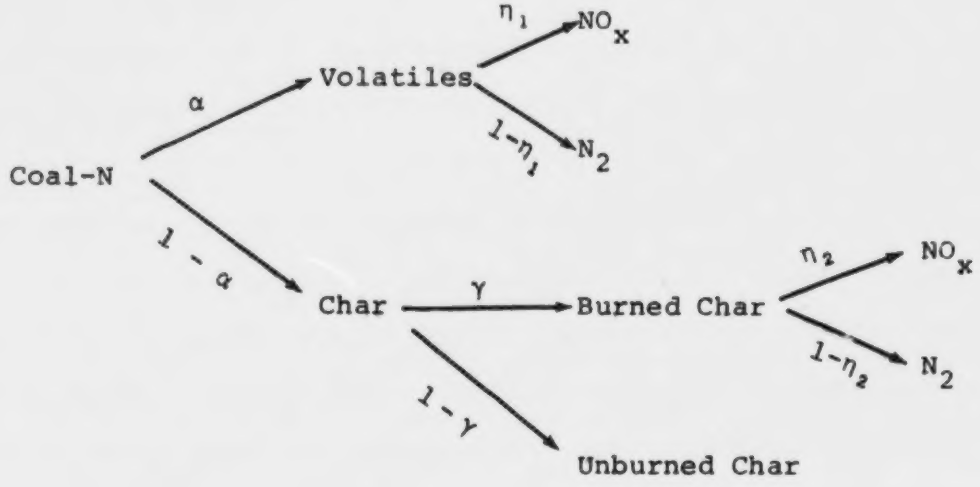
Most coal burned for power generation is done so in large unit pulverized coal flames (hundreds of megawatts of electrical capacity). In such combustors, coal, ground to a particle size of less than 200 microns, is injected through a nozzle into a region of preheated air where the particles are rapidly heated by conduction and radiation in about 1 millisecond to temperatures of 2000°K or higher. During the next tens of milliseconds, volatile matter is evolved which undergoes homogeneous gas phase oxidation in a mode intermediate to premixed and diffusion flames. Burning of the volatile matter is usually complete in about 10-100 milliseconds. Simultaneously, the devolatilized or partially devolatilized char undergoes heterogeneous oxidation. Char burnout is usually complete in about 300 milliseconds.

Coal combustion can thus be conceptualized as rapid heating causing devolatilization, followed by two distinctly different (and, to first approximation, independent) elementary oxidation mechanisms. Clearly, emission of any combustion product, in particular, NO_x, is affected by the relative rates and efficiencies of all three aforementioned physical processes, each of which, in turn, is differently affected by alteration of any of the parameters accessible to the combustion engineer, e.g. heating rate, temperature, fuel/air equivalence ratio, degree of mixedness, residence times, etc.

It is certainly not clear, *a priori*, what combinations of conditions will lead to minimization of product emissions, especially trace pollutants whose fundamental formation paths are not, in any case, well characterized. It is obvious, therefore, that systematic development of an optimum combustion modification strategy designed to minimize NO_x emissions without otherwise adversely affecting combustor operation awaits an understanding of the coupled physical and chemical mechanisms by which fuel-nitrogen is converted to NO_x.

Ideally, a full mechanistic exposition of the problem would entail a microscopic or molecular description of the pathway by which fuel-nitrogen is converted to NO_x. This would, in principle, start with the thermal or catalytic rupture of specific bonds in the carbonaceous coal matrix leading to well-characterized pyrolysis products, followed by parallel homogeneous and heterogeneous oxidative routes described in the former case by numerous coupled, elementary reactions and in the latter case by consideration of surface and pore transport effects as well. Unfortunately, development of such a fundamental mechanism of fuel-nitrogen conversion is yet rather distant, and, given, among other problems, the current dearth of necessary rate data, only marginally tractable at present.

These considerations, however, do not preclude the possibility of characterizing the various steps of fuel-nitrogen conversion in a somewhat more phenomenological vein, while retaining a quantitative sense of "mechanism" adequate to the needs of the fuels engineer. That is, the routes by which fuel-nitrogen is converted to either NO_x or N_2 (the desired end product) may still be mechanistically traced, and, at each juncture, the influence of systematic variation of combustion parameters may be quantitatively examined. This more empirical mechanism of coal-nitrogen conversion may be described as follows:


Coal-N
α
Volatiles
η_1
NO_x
$1-\eta_1$
N_2
1 - α
Char
γ
Burned Char
η_2
NO_x
$1-\eta_2$
N_2
1 - γ
Unburned Char

This study focusses on the conversion of fuel-nitrogen in pulverized coal flames for two representative United States coals, a Pittsburgh Seam bituminous and a Montana lignite. Each essential step in the empirical mechanism has been quantitatively investigated with respect to variation of combustion parameters and / or reaction rate. The results are applied qualitatively to the development of a staged combustion process designed to minimize NO_x emissions. Quantitative results, essential to the design of such a combustor, are presented.

SECTION II

BACKGROUND

The formation of nitrogen oxides during coal combustion is a complicated process involving contributions both from the fixation of atmospheric nitrogen (thermal NO_x) as well as from the oxidation of nitrogen bound chemically in the fuel (fuel NO_x). It is, primarily, to the latter of these two processes that this study is directed. For an excellent review of the literature through mid-1976, the reader is further referred to Pershing (1976).

It is recognized that combustion of pulverized coal particles occurs in three main stages: evolution of the volatile components or devolatilization, followed by homogeneous volatile combustion, and, finally, heterogeneous combustion of the residual char. Although the stages may overlap to some degree (Howard and Essenhigh 1967a, 1967b), it is clear that char combustion is generally of much longer duration then volatile combustion. Based on this model, the conversion of coal-nitrogen to NO_x can,therefore, also be regarded as a three-stage process: coal-nitrogen devolatilization, volatile-nitrogen combustion, and char-nitrogen combustion. It is evident that the extent of devolatilization prior to ignition and the distribution of nitrogen between char and volatiles will strongly influence NO_x emissions. Finally, since the destruction of NO_x is as important as the formation of NO_x in determining the net NO_x emission from a coal combustor, a review on the reduction of NO_x by char is also included.

II-1 FUEL NO AND THERMAL NO

An early investigation of the production of NO during fluidized bed combustion of coal was reported by Jonke, et al (1970). In their experiment, after steady-state combustion had been reached with a synthetic air mixture of nitrogen and oxygen, argon was substituted for the nitrogen. It was found that the NO level of the flue gas was not materially affected by the substitution of argon for the nitrogen. This indicated that the major source of nitrogen for the production of NO was the nitrogen bound chemically in the coal. This conclusion, while establishing the significance of fuel-NO, did not, however, rule out the possibility of significant contributions from thermal NO under the higher temperature conditions of pulverized coal flames. (Thermal NO, known to be formed via the highly temperature sensitive Zeldovich mechanism (Zeldovich 1946), is not expected to contribute significantly under the low temperature conditions of a fluidized bed combustor.)

Pershing (1976) and Pershing and Wendt (1976) isolated fuel NO by using, instead of air, a synthetic oxidant mixture of the same heat capacity containing 21% O_2, 18% CO_2, and 61% Ar. Comparison between total NO with preheated air as the oxidant and fuel NO with synthetic mixture as the oxidant was accomplished under nearly identical combustion conditions. From the studies of four different coals and one coal char, they found that, typically, fuel NO contributed over 80% of the total NO emissions. In addition, they also concluded that fuel NO formation is relatively insensitive to flame temperature over a wide range of practical interest.

The reaction mechanism for the formation of thermal NO from the fixation of atmospheric nitrogen was first proposed by Zeldovitch (1946). This mechanism has since been confirmed and modified by a number of investigators. The Zeldovitch mechanism is highly temperature dependent so that in typical laboratory scale pulverized coal flames, little thermal NO is expected due to the comparatively low flame temperatures of small-scale combustors with cold walls. This explains why little thermal NO has been observed and why fuel NO contributes most of the total NO emission in small-scale coal-fired systems.

II-2 CHAR NO AND VOLATILE NO

Until now, very little quantitative information has been available on the relative contributions to fuel NO_x emissions of the nitrogen evolved from the coal as volatiles (and oxidized homogeneously) and the nitrogen retained in the char (and oxidized heterogeneously). In addition, no information is available in the literature on the pyrolysis of nitrogen from coal at pulverized coal flame conditions, although some data are available on the distribution of the nitrogen in coal among pyrolysis products at coking conditions. The coking data, however, are not applicable to pulverized coal flames because of differences in heating rates, final temperature, residence times, and particle interactions.

Based on these fragmentary data, Sternling and Wendt (1972) drew up a scheme for the distribution of coal nitrogen between volatiles and char during pyrolysis and oxidation. They indicated that a significant portion of the nitrogen in the coal would not be volatilized but would remain in the char, so the oxidation of nitrogen in the char might contribute significantly to NO emissions.

Coal char combustion is a very complicated process. Since the char structure is porous, both internal and external combustion occur. (Anson, Moles, and Street, 1971). In addition, pore diffusion may sometimes play an important role in the combustion process (Mandel 1977).

The physical and chemical characteristics that influence the conversion of fuel nitrogen to NO_x during coal char combustion were further examined theoretically by Wendt and Schulze (1976).

They showed that diffusion-reaction interactions are important in determining the selectivity of the char particle toward nitric oxide production. Their model predicts that char combustion is a potentially high source of NO.

The work by Blair _et al_.(1976) has also shown that a large fraction of the nitrogen may remain in the char after devolatilization. Studies of the behavior of fuel-nitrogen under simulated combustion conditions by Pohl (1976), Pohl and Sarofim (1976), and Song, Beér, and Sarofim (1977) also support this picture for temperatures below 1750°K, but the trend of the data suggests that much of the fuel nitrogen may be devolatilized at higher temperatures.

In a study utilizing a fluidized bed combustor, Pereira and Beér (1975) and Pereira (1975) have assessed the influence of temperature on the relative contributions of char-nitrogen and volatile nitrogen to the total NO emissions. They showed that the char contribution to the total NO emissions predominated at low temperatures (800°C and less), whereas at higher temperatures the contribution of the volatile fraction became more important.

It is useful to indicate the similarity between the combustion of coal-volatiles and ordinary gaseous flames. The volatile combustion process may be generally regarded as proceeding in two stages: first, the volatiles must mix with oxygen, and secondly, chemical reaction must occur. It is apparent that the combustion of coal volatiles is analogous to ordinary gaseous flames. It is easiest to investigate kinetic mechanisms in systems that have uniform mixing, consequently much laboratory work has been done on the conversion of simple nitrogen compounds in premixed, gaseous hydrocarbon flames.

The earliest relevant flame study, performed by Shaw and Thomas (1965), is only historically significant and the data must be reinterpreted to include in the fuel equivalence ratio the amount of oxygen necessary to burn the nitrogen additive. Subsequent studies by Fenimore (1972), De Soete (1973), and Sarofim, Williams, Modell, and Slater (1975) have, however, resulted in the following generalizations:

1. The conversion of fuel-nitrogen to NO_x is close to quantitative under fuel lean conditions, but decreases dramatically for fuel rich conditions,
2. An increase in fuel nitrogen concentration results in an increase in total NO_x emissions but a decrease in the conversion efficiency to NO_x, and
3. Conversion efficiency increases slightly with increasing flame temperature.

These conclusions, derived from studies on idealized laboratory systems, are also supported by the results obtained on practical industrial systems (Martin and Berkau, 1972; Turner _et al_., 1972; and Bartok _et al_., 1972).

II-3 REDUCTION OF NO BY CHAR

In an experimental effort to investigate the NO_x emissions from a fluidized bed coal combustor, Gibbs, Pereira, and Beér (1976), observed a reaction between NO and char. Although char was known to react readily with NO in the absence of oxygen (Edwards, 1972), an NO-char reaction had not, previously, been predicted under oxidizing conditions. An investigation was then conducted to study the reaction between NO and char in a fluidized bed operating over a temperature range of approximately 600°C to 900°C. They reported that the reaction had a relatively low activation energy (∿16 Kcal/mole) and a reaction order of one with respect to NO. In addition, they also found that the nitric oxide reduction was strongly dependent on the char particle size, with increasing conversion as particle size decreased.

These conclusions are partially supported by the recent work done in Japan (Furusawa, Kunii, Oguma, and Yamada, 1977). The Japanese researchers have conducted a kinetic study of NO_x reduction in a fixed bed reactor with a dilute mixture of carbonaceous materials (i.e., char or activated carbon) over a wide range of temperatures (750-1250°K). They also found that the reduction of NO_x was first order with respect to NO_x concentration. Interestingly though, they observed three temperature ranges with different activation energies: 17.3 Kcal/mole for 773°K to 993°K; 57.1 Kcal/mole for 993°K to 1056°K; and 39.7 Kcal/mole for 1056°K to 1183°K.

Apparently, the char/NO_x reaction is analogous to the char/O_2

reaction, and in fact, NO may compete with O_2 for the char gasification reaction. It is important to consider the NO/char reaction in determining net NO_x emissions from a coal combustor. A better understanding on the NO/char reaction will, of course, provide information pertinent to the reduction of NO_x emission by the modification of the combustion processes.

SECTION III

EQUIPMENT AND PROCEDURE

The equipment to be described has been developed for use in several coal research projects in M.I.T.'s Fuels Research Laboratory. The equipment was designed to cover experimental conditions of interest for pulverized coal flames and can simulate the extremely rapid heating expected in the pulverized coal flame; for example, data has been taken on coal devolatilization, in a dispersed phase, with time resolution of about 0.5 milliseconds, heating rate of about 2 x 10^5°K/sec, and a maximum temperature of 2100°K. Experimental conditions of gasifiers are of secondary interest and have not been matched nearly so well.

III-0 FLOW FURNACE

Flow reactors have been used widely by various researchers. Kimber and Gray (1967) applied such a system to coal studies at temperatures up to 2800°K. One of the main advantages of flow furnaces is the similarity to actual systems. By controlling both gas and wall temperatures, a wide range of simulation is possible, and the results may be readily applicable to real systems. A typical flow furnace system includes a temperature controlled furnace, a high temperature gas supply device, a coal feeder, and a sampling probe. The relative complexity of the system and material problems at high temperatures are major detriments of such an apparatus.

For the present study, a laminar flow furnace was chosen for its versatility. Similar systems were developed by BCURA researchers (Field, 1970 and Badzioch and Hawksley, 1972), but some important improvements were made in system designs and characterizations. These improvements include a partially fluidized vibrating feeder, a water-quenched collector with a bronze filter and particle velocity measurements by a laser doppler anemometer. In the BCURA studies, char particles were quenched by thermal conduction from water cooled collector walls and then separated by cyclone separators. Good recovery of particles was not achieved because of the adhesion of char particles to the collector wall. In the present study this problem is solved by collecting char particles with a bronze filter at the mouth of the collector. Water or argon is injected at the mouth of the collector in order to quench the coal particles rapidly.

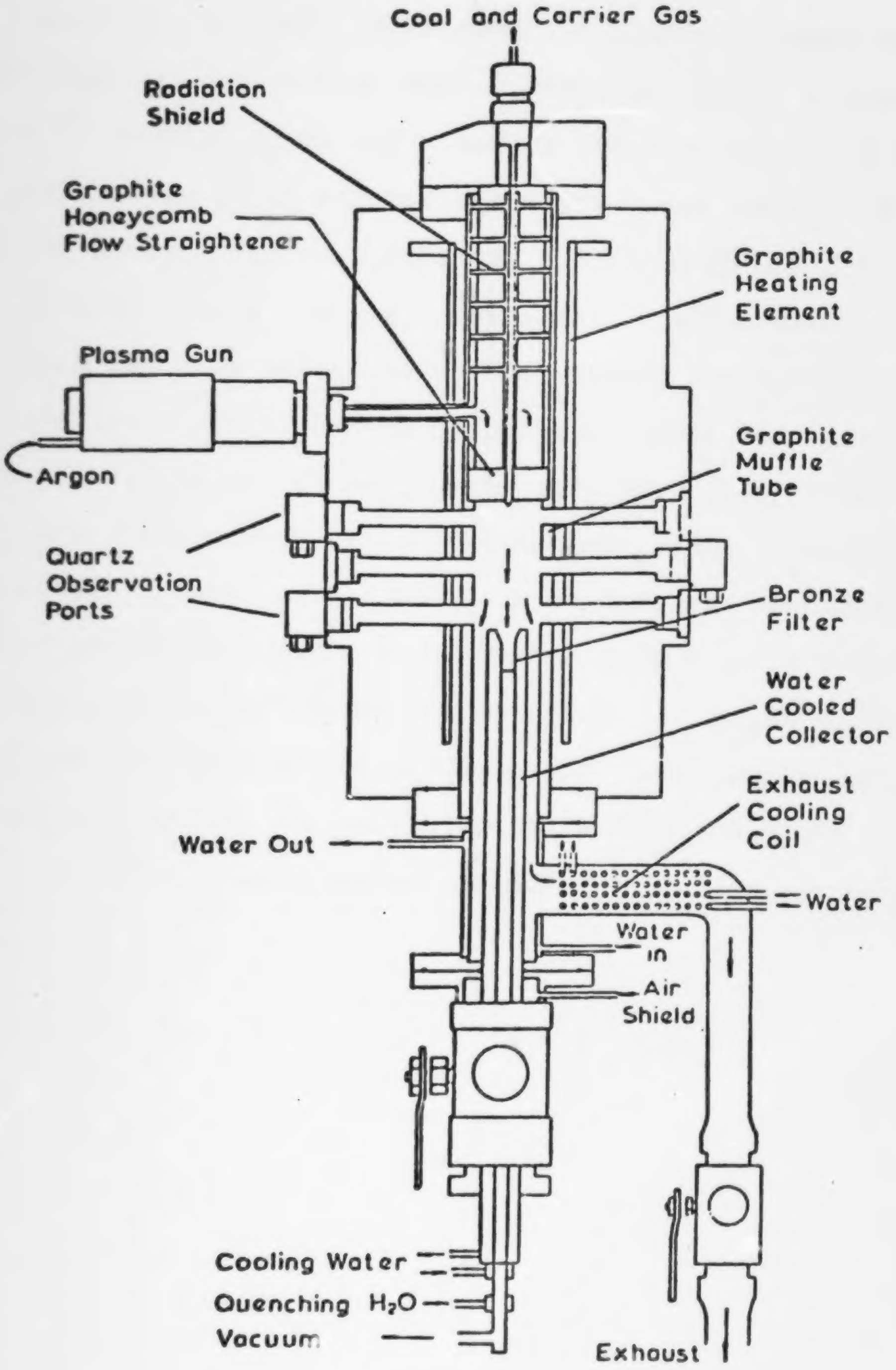
III-1.0 PYROLYSIS EXPERIMENT

The objective of the pyrolysis experiments is to elucidate the mechanism and rate of nitrogen devolatilization from coal. Regulation of the evolution of nitrogenous volatiles is of major importance in the control of nitric oxide emission.

III-1.1.0 LAMINAR FLOW EXPERIMENTS

A schematic of the laminar flow furnace system is shown in Figure III-1. The system is built around a modified ASTRO model 1000A graphite furnace (ASTRO Industries, Inc., Santa Barbara, California). A 3.5 in. I.D., 12 in. long graphite resistance heating element is used to control furnace temperatures. A 4 in. I.D. graphite radiation shield and packed graphite powder provide thermal insulation. The outer shell is about 11 inches in diameter and water-cooled for easy access. The furnace is equipped with a programmed automatic temperature control which allows temperature changes to be made at desired rates. This feature is especially important when ceramic muffle tubes are used, since they are susceptible to thermal shock. The temperature is controlled through a tungsten-rhenium thermocouple which is located just outside the heating element in the center of the furnace. The maximum operating temperature of the furnace is about 3000°K with a graphite muffle tube. Three pairs of observation ports are located along the axis of the furnace at intervals of 1.5 inches. The ports have quartz windows which supply an observation area of 0.5 in. in diameter. Optical instruments such as a radiation pyrometer or a laser doppler anemometer are used through these windows. Coal particles are injected into the center of the 2 in. I.D. graphite muffle tube through a 0.047 in. I.D., 3/16 in. O.D. water-cooled stainless steel injector. A 5/8 in. O.D. graphite tube is used as a heat insulator to minimize the heat loss to the water-cooled injector. Preheated gas is introduced horizontal to the axis of the furnace and

FIGURE III-1.


Coal and Carrier Gas
Radiation Shield
Graphite Honeycomb Flow Straightener
Graphite Heating Element
Plasma Gun
Argon
Graphite Muffle Tube
Quartz Observation Ports
Bronze Filter
Water Cooled Collector
Exhaust Cooling Coil
Water Out
Water
Water in
Air Shield
Cooling Water
Quenching H₂O
Vacuum
Exhaust

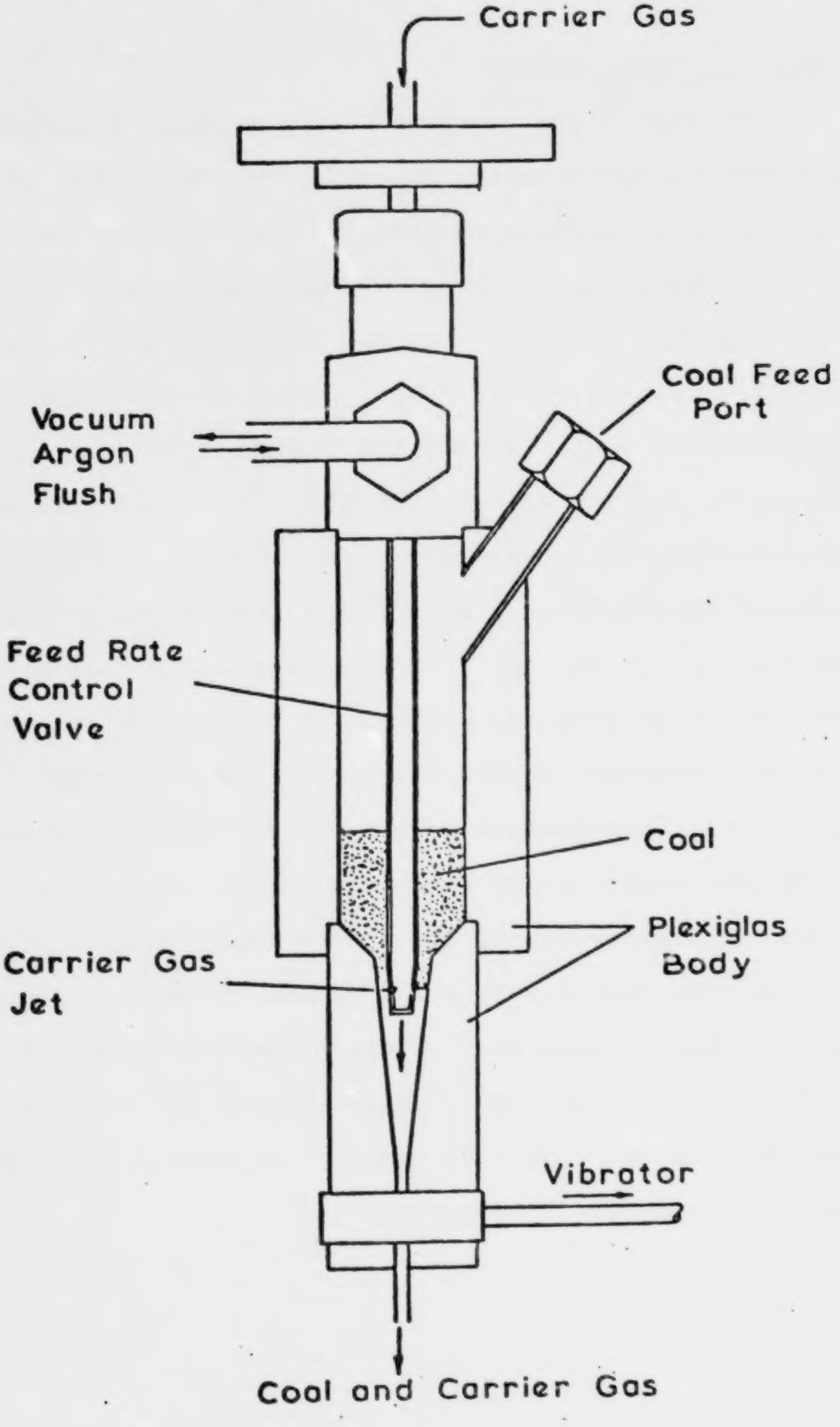
LAMINAR FLOW FURNACE SYSTEM

straightened through a 1 inch thick graphite honeycomb. The honeycomb holes are 0.067 inches in diameter and the distance between holes is 0.083 inches. The lower surface of the honeycomb is 0.5 inches above the center of the first observation port. Six 2-3/8 inch disks are placed 1 inch apart above the honeycomb to prevent radiant heat loss. The coal particles are heated as the carrier gas mixes with the preheated main gas flow. The char is collected in a water-cooled bronze filter after being quenched by water jets. The rest of the gas is cooled by an exchanger and exhausted. Since the muffle tube is constructed from graphite, atmospheric air must be excluded at all times. Two ball valves provide a convenient method for quickly closing the passages through which the collector is removed or for shutting off access to the plasma gun. The graphite muffle tube and the honeycomb are replaced by an alumina muffle tube and an alumina honeycomb for experiments in oxidizing atmospheres.

III-1.1.1 COAL FEEDER

The coal feeder (Figure III-2) employs a mechanical vibrator and partial fluidization of coal particles. The combined system results in relatively uniform feed rates. The main body is made of polished plexiglas which allows observation of the coal level and feed rate. The I.D. of the plexiglas section is 0.5 inches and the length 3 inches; about 5 gm. of coal can be charged. The feed rate is controlled by the needle valve opening, the vibrator strength, and the carrier gas flow rate. The carrier gas is introduced through the hollow needle valve and injected radially through four equally spaced, 0.010 inch holes at the tip of the needle valve. The gas fluidizes the coal particles locally, thus preventing packing and clogging in the narrow region. An external electric vibrator shakes the entire feeder assembly. The exit of the feeder is connected to a 0.065 in. O.D. and 0.047 in. I.D. stainless steel tubing which vertically enters the furnace. The vertical arrangement of the feeder-injector line allows the use of a fine tube with a very small amount of carrier gas flow (as small as 5 cc/min). Less carrier gas allows more rapid heating of the injected particles. Feed rates between 0.01 gm/min and 1.0 gm/min can be obtained with reasonable uniformity. In normal operations about 0.15 gm/min is used.

FIGURE III-2.

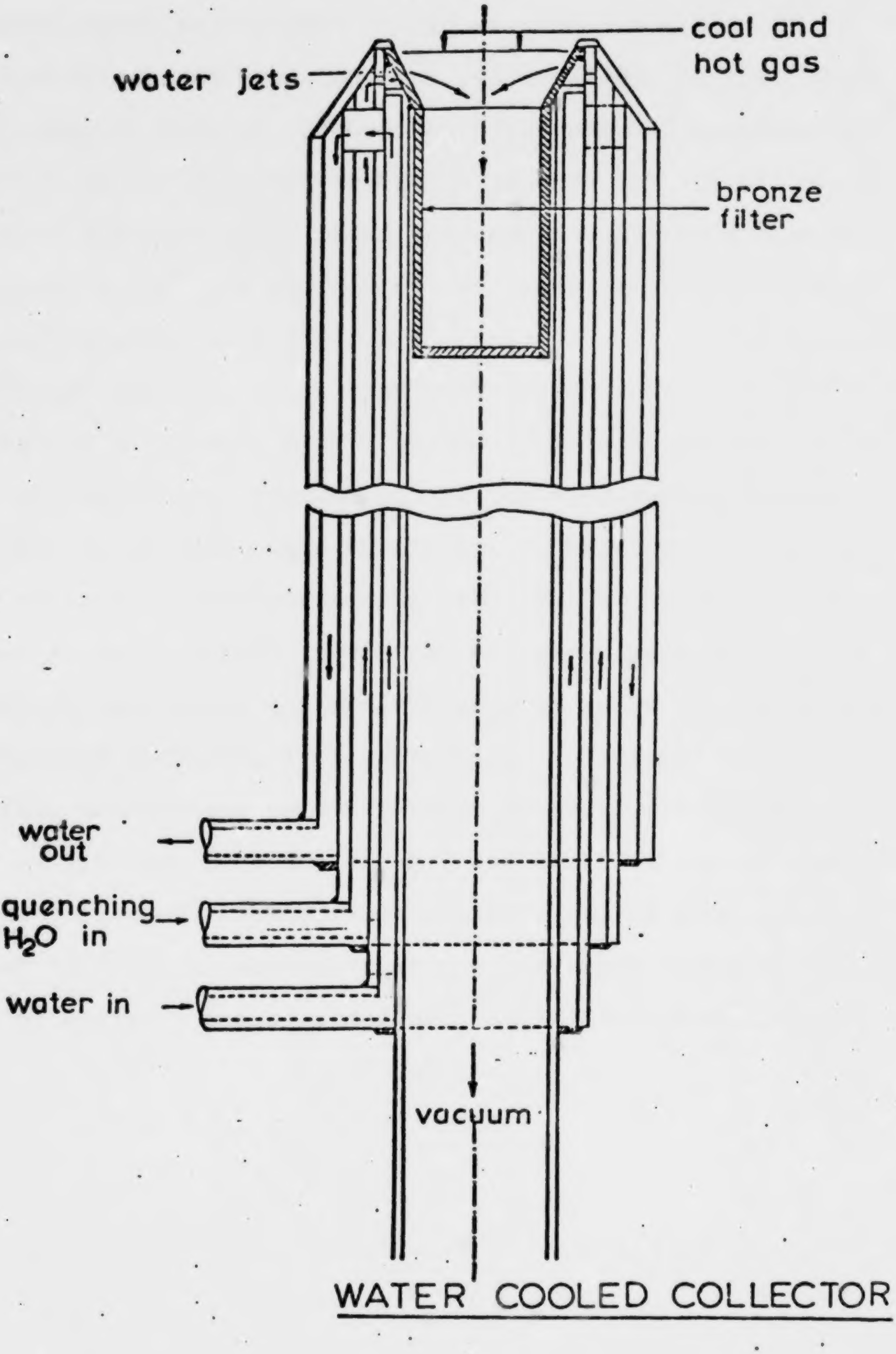

Carrier Gas
Vacuum
Argon
Flush
Coal Feed
Port
Feed Rate
Control
Valve
Coal
Plexiglas
Body
Carrier Gas
Jet
Vibrator
Coal and Carrier Gas

COAL FEEDER.

III-1.1.2 PARTICLE COLLECTOR

The collector (Figure III-3) consists of three concentric copper tubes. The external cooling water passes through two of the passages and the third is used to withdraw the quenched gases. Eight 1/8 in. O.D. copper tubes pass through the second water passage to carry the quenching water to be directly injected. Heat transfer analysis shows that cooling by conduction to the water-cooled wall is insufficient to achieve char quenching because of the relatively large hot gas flow rate (up to 1ℓ/sec) and the necessarily large collector diameter. This problem is solved by directly injecting quenching water at the mouth of the collector through twelve holes drilled in the flared upper section of the sintered bronze filter. (The filters are manufactured specially by Thermet Inc., Gloucester, Mass.). The porous bronze filter allows some of the quenching water to pass through the whole area of the upper section of the filter, preventing coal particles from adhering and being exposed to intense radiation from the furnace wall. The bronze filter is 0.740 in. O.D. at the open end, 0.4 in. O.D. and 4 inches long at the straight section, and the wall thickness is 0.060 inches. The average size of bronze is about 15 microns and coal particles larger than 5 micron are retained in the filter.

FIGURE III-3


coal and hot gas
water jets
bronze filter
water out
quenching H_2O in
water in
vacuum

WATER COOLED COLLECTOR

III-1.1.3 GAS PREHEATER

An AVCO plasma gun model PG 040 is attached to the furnace to preheat the main gas stream. The plasma gun has a water-cooled copper anode. An AIRCO model 1500-C7 welding rectifier supplies D.C. power to the gun. The maximum power input to the plasma gun is 40 Kw. The plasma heats the gas with a 30 percent thermal efficiency. The temperature of the preheated gas is controlled by changing the power input and the gas flow rate. Argon, helium, nitrogen or hydrogen can be used as working gases. A graphite muffle tube restricts the working gas, therefore only inert gases can be used.

III-1.1.4 SUCTION SYSTEM

A mechanical vacuum pump is used to withdraw the injected quenching water and the quenched argon gas. Water is separated from the gas by a gravitational separation vessel. The quenched gas is dried through a packed bed of calcium sulfate and metered by a Fischer and Porter flowmeter.

III-1.1.5 EXPERIMENTAL PROCEDURE

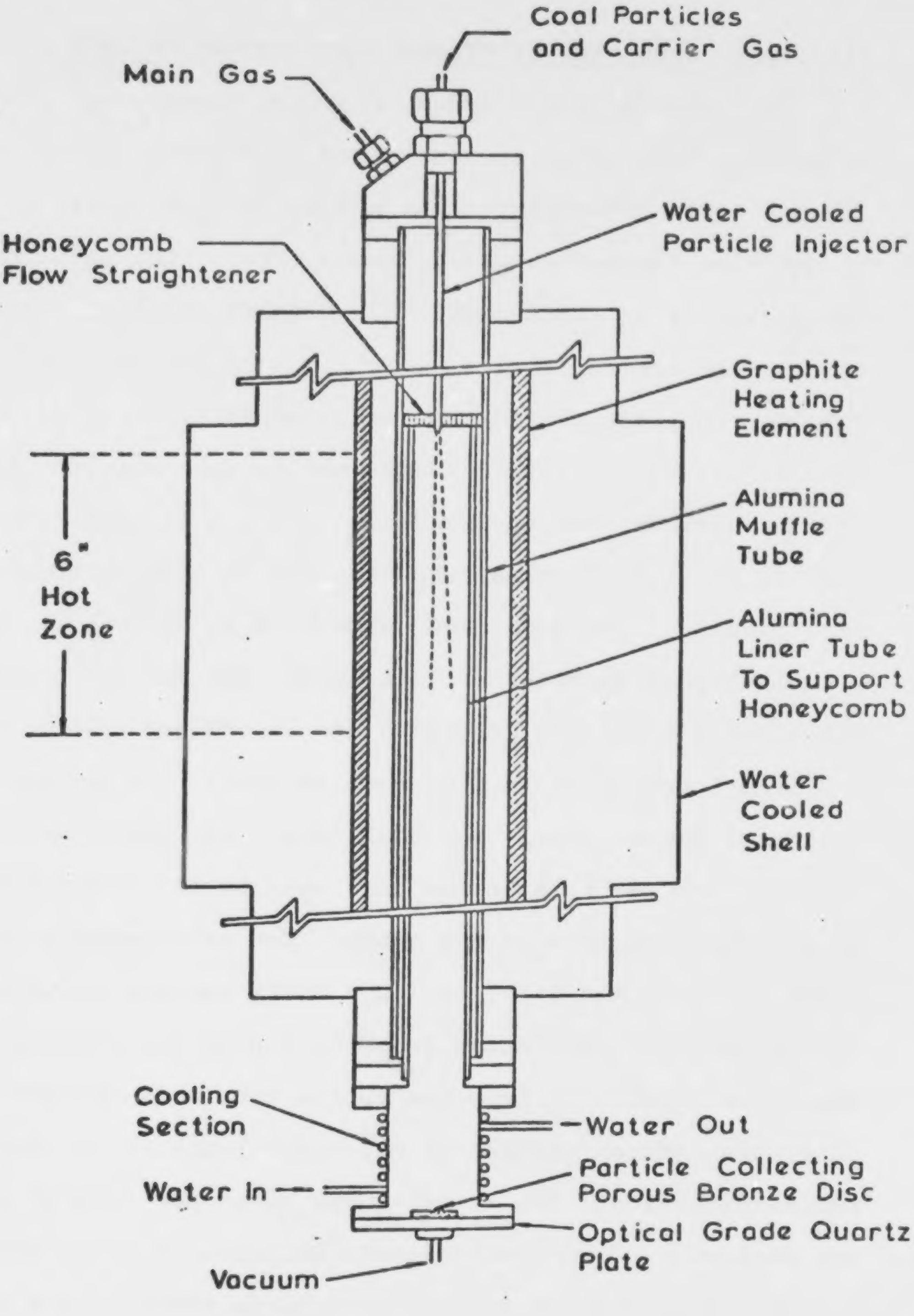
The furnace is heated to a desired temperature using the automatic temperature controller. Three tungsten-rhenium thermocouples, introduced through the observation ports, are used to monitor the temperature inside the muffle tube. After steady-state is reached, the main gas is introduced and the plasma gun is started. The temperature of the main gas is controlled to the same temperature as the furnace wall temperature. This is done by matching the thermocouple readings before and after the introduction of the main gas. The main gas flow rate is controlled by a Fischer and Porter flowmeter to give desired main gas velocities. The pressure of the furnace is maintained at about 2 inches of water.

A predried bronze filter is weighed and placed in the collector. Suction rates vary between 1/3 and 1/2 of the main gas flow rates depending on the furnace temperature. The flow rate of the quenching water jets is maintained at 0.7 ℓ/min for most runs. After a desired suction rate and a water flow rate are obtained, the collector is raised into the furnace and positioned at a prescribed distance from the coal particle injector. About 0.05 to 0.5 gm of coal is weighed and charged into the feeder. Then, a carrier gas flow rate and a needle valve opening are set and the vibrator is turned on. The coal level in the feeder is continuously monitored. As char particles accumulate in the bronze filter, a cake builds up. In order to maintain the same suction rate, the valve opening of the suction line has to be increased to compensate for the increased pressure drop across the filter. The maximum pressure drop allowed is about 20 in. Hg. Upon completion of the coal particle injection, the collector is removed from the furnace and replaced with a new bronze filter. The collector is raised again to a different location and the next run is started. Normally about ten runs are repeated at the same experimental conditions with different collector locations. After all runs are finished, the filters are dried at 110°C for three hours in a nitrogen atmosphere. The filters are then cooled in a desiccator and weighed as soon as the room themperature is reached. Char samples may be analyzed for ash content or sent to Galbraith Laboratories, Inc., Knoxville, Tennessee for the ultimate analysis. Weight loss of coal is determined by the difference of the weights between the coal fed and the collected char.

III-1.2.0 FREE FALL EXPERIMENT WITH BRONZE COLLECTOR

In order to obtain longer reaction times, coal particles are allowed to fall under the influence of gravity through a preheated furnace. The schematic of the system (Figure III-4) is similar to the flow furnace shown in Figure III-1. The main component of the system is an ASTRO model 100A graphite furnace. The same temperature control system, which is used for the laminar flow furnace, controls the furnace wall temperature. A 24 inch long, 3 in.O.D., 2 1/2 in.I.D. alumina muffle tube shields the graphite heating element from the reaction zone. A 15 inch long, 2 1/4 in. O.D., 2 in. I.D. alumina tube supports an alumina honeycomb flow straightener. The honeycomb, made by E.I. du Pont de Nemours, has a nominal pore diameter of 1/16 inch. The maximum temperatures of the alumina tubes and honeycomb are 2100°K and 1900°K respectively. A 9 inch long, 3 1/2 in.I.D. cooling section is attached to the bottom of the furnace. The coal feeder and the water-cooled injector are the same as the ones used in the laminar flow system, except the diameters of the tubes. The water-cooled injector is 0.250 in. O.D. and 0.101 in.I.D. Small amounts of main gas (about 0.05 ℓ/sec) are introduced from the top of the furnace. The gas is heated by conduction from the muffle tube wall and honeycomb. The honeycomb induces uniform velocity and temperature profiles in the radial direction. The temperatures along the axis of the furnace are measured by a chromel-alumel thermocouple up to 1500°K and by a platinum-rhodium or an iridium-rhodium thermocouple above 1500°K. Since the main gas Reynolds number is small, the flow is practically

FIGURE III-4.


Coal Particles and Carrier Gas
Main Gas
Water Cooled Particle Injector
Honeycomb Flow Straightener
Graphite Heating Element
6" Hot Zone
Alumina Muffle Tube
Alumina Liner Tube To Support Honeycomb
Water Cooled Shell
Cooling Section
Water Out
Particle Collecting Porous Bronze Disc
Water In
Optical Grade Quartz Plate
Vacuum

FREE FALL EXPERIMENT WITH BRONZE COLLECTOR fully developed for the entire region. Therefore the temperature of the main gas is considered to be close to the wall temperature of the muffle tube. Coal particles are introduced into the center line of the main flow through the water-cooled injector. Carrier gas flow rates between 2 cc/min. and 25 cc/min. are used. Char particles are collected on a 3 inch diameter, 1/8 inch thick sintered bronze disk at the bottom of the cooling section. The bronze discs are manufactured by Thermet, Inc., Gloucester, Mass. They have an average pore diameter of about 5 microns. The gas exits through a 1/4 inch pipe fitting under the center of the bronze disc.

III-1.2.1 EXPERIMENTAL PROCEDURE

The furnace is heated to a desired temperature at a heating rate between 250°C/hr. and 350°C/hr., using the temperature programmer. After a steady state is reached, a preweighed bronze filter is placed on the bottom flange. Then the furnace is alternatively evacuated and filled with argon several times to eliminate atmospheric air. About 1 gram of coal is weighed and charged to the feeder. The suction rate is controlled so that the furnace pressure is maintained at atmospheric pressure for fixed main gas and carrier gas flows. The vibrator is started and coal is fed in about 10 minutes, giving a feed rate of 0.1 gm/min. After all the particles are fed, the bronze disc is removed and quickly weighed to avoid adsorption of moisture. The collected char is transferred to a sample bottle for analyses, such as ash content, elemental composition, and particle size distribution.

III-1.2.2 FREE FALL EXPERIMENT WITH ALUMINA COLLECTOR

The object of this experiment is to obtain the asymptotic weight loss values at high heating rates and very long reaction times. The furnace is the same as used in the free fall experiment with the bronze filters. A 40 mm. O.D., 165 mm. long cylindrical alumina crucible (Coors CN-170) is supported by a 1 7/8 in. O.D., 3/8 in. I.D. alumina tube. A thermocouple is placed between the support disc and the bottom of the collector to monitor the temperature during the experiment. The crucible temperature is recorded continuously on a chart recorder. The collector is raised or lowered by a motor-driven linear actuator at a constant speed. This is to protect the ceramic material from thermal shock caused by a sudden temperature change. At 1830°K it takes about 20 minutes to position or remove the alumina collector.

III-1.2.3 EXPERIMENTAL PROCEDURE

After a desired furnace temperature is attained, a preweighed alumina collector is raised to the hot zone of the furnace by the linear actuator. The furnace is continuously purged by argon to prevent contamination by air leaks. The temperature at the bottom of the collector is recorded and when a steady state is reached, about 1 gram of coal is fed in approximately 10 minutes. Main gas flow rates between 0 and 0.05 ℓ/sec and carrier gas flow rates between 2 cc/min. and 24 cc/min are used. After all the particles are fed, the collector is kept for 10 minutes at the same position in order to assure sufficient reaction time for the particles fed last. The collector is then lowered into the cooling section and transferred to a desiccator. About half of the char sample and the material left in the crucible are analyzed for ash content.

III-1.3.0 CRUCIBLE EXPERIMENT

The object of the crucible experiments is to determine weight loss under slow heating conditions and extremely long residence times. Instead of feeding and collecting coal particles, as in the case of free fall and laminar flow experiments, about 1 gram of coal is weighed and placed in a 15 mℓ alumina crucible (Coors CH-16), then the crucible is raised into the hot zone of the furnace using the linear actuator discussed above. The temperature between the crucible and the support disk is recorded by a thermocouple during the whole cycle of heating and cooling. Heating rates between 0.5°K/sec and 5.0°K/sec can be obtained. It should be noted that this experiment is close to the ASTM proximate analysis for the determination of volatile matter, where one gram of coal is placed in a 15 mℓ platinum crucible, lowered into a furnace heated to 950°C, and held for seven minutes.

III-1.3.1 EXPERIMENTAL PROCEDURE

The procedure is the same as that of the free fall experiment with alumina collector, except no coal if fed.

III-2.0 OXIDATION EXPERIMENTS

Two types of oxidation experiments serving two different purposes have been performed, the former a coal or char oxidation experiment at a fixed residence time of one second (free fall mode), the latter a time-resolved char oxidation experiment (laminar flow mode). The objective of the fixed residence time experiments is to investigate the conversion of fuel nitrogen to nitrogen oxides under different burning conditions. Comparison of coal and char oxidation results (See Section VI-3) enables the separate contributions to NO_x emissions of volatiles and char to be identified. Variables of greatest interest which are investigated are flame temperature and fuel equivalence ratio. The distribution of nitrogenous products in the gas phase and condensed phase are of particular interest for the evaluation of the contribution of fuel nitrogen to noxious bound nitrogen products. The objective of the time-resolved experiments is to determine the kinetics of char oxidation with a view towards establishing residence time requirements for completing char burnout and to further determine the fate of fuel nitrogen undergoing heterogeneous oxidation.

III-2.1.0 FREE FALL EXPERIMENT

Coal and coal char oxidation experiments at a fixed residence time of one second are run in the alumina muffle tube furnace in free fall mode as described in Section III-1.2.0. The coal-char used in these studies is prepared by pyrolysis of the coal at the temperature and residence time corresponding to those of the oxidation experiments. Either air or a helium-oxygen mixture, simulating air, is used as the oxidizing atmosphere in all oxidation experiments.

III-2.1.1 EXPERIMENTAL PROCEDURE

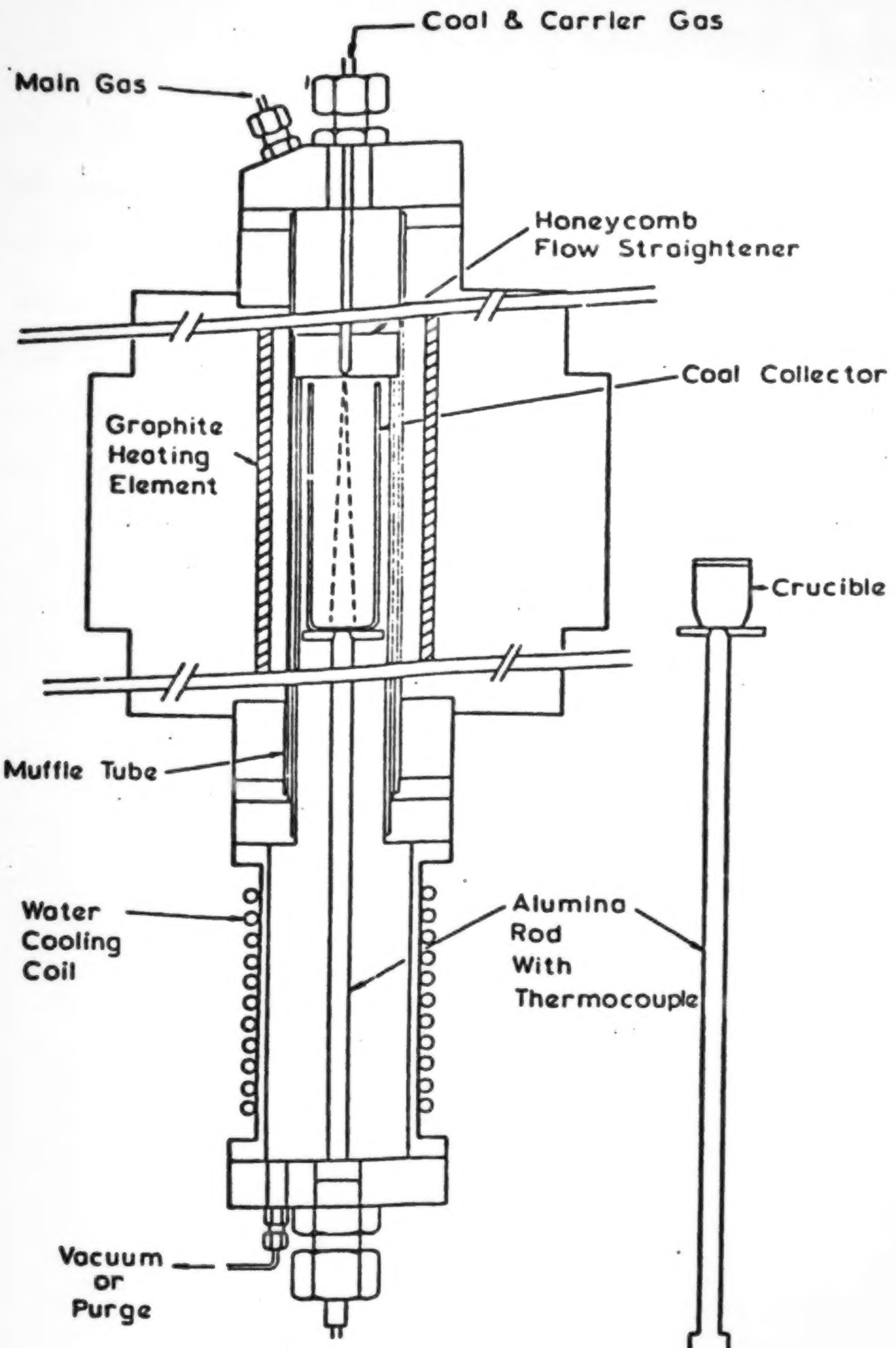
The experimental procedure is the same as that described in Section III-1.2.1 except that an oxidizing gas is now introduced into the furnace as the main gas. The main gas flow is typically on the order of 3000 cc/min. A small amount of additional oxidizing gas, about 30 cc/min., is used to carry the coal into the furnace. These conditions result in a small flame stabilized on the injector nozzle. The flame length depends somewhat on operating conditions, but is typically about two inches long. Large amounts of soot and unburned coal are observed leaving the flame under fuel rich flame conditions, but only ash is recovered under lean conditions. The furnace wall temperature is controlled in the manner described previously. The wall temperature is measured both with an optical pyrometer and with thermocouples. Nitric oxide concentrations are measured with a chemiluminescence NO meter from a slip stream of the total gas flow out of the furnace (See Section III-4).

Quenched char and condensable material are collected at the bottom of the furnace on a porous sintered bronze disk. The recovered material is weighed to determine the percent of the material burned and some samples are sent to Galbraith Laboratories, Inc., Knoxville, Tennessee for nitrogen analysis by the Kjeldahl procedure.

III-2.2.0 LAMINAR FLOW EXPERIMENT

The alumina muffle tube furnace described in Section III-1.2.0 can also be used in a laminar flow mode by removing the water-cooled bottom section and adding water-cooled flanges for the accommodation of a water-cooled probe. A schematic of the experimental apparatus is shown in Figure III-5. This alumina muffle tube laminar flow furnace is similar to the graphite muffle tube laminar flow furnace described in Section III-1.1.0, except for the differences in particle collector, gas preheater, and suction system.

FIGURE III-5.


Coal & Carrier Gas
Main Gas
Honeycomb Flow Straightener
Coal Collector
Graphite Heating Element
Crucible
Muffle Tube
Water Cooling Coil
Alumina Rod With Thermocouple
Vacuum or Purge

FREE FALL EXPERIMENT WITH ALUMINA COLLECTOR AND CRUCIBLE EXPERIMENT

III-2.2.1 PARTICLE COLLECTOR

The collector probe is essentially the same as the one described in Section III-1.1.2. However, as the furnace studies have progressed, the water quench initially used was dropped in favor of a gas quench for the following reasons:

1. With water quenching, the bronze collecting filter quickly becomes clogged, probably due to the tendency of water to wash small ash particles off the char surface into the filter pores. With gas quenching, there has been no sign of filter clogging.

2. Use of a gas quench simplifies the experimental apparatus. With only gases, but no water, evolved from the furnace, the large reservoir required to separate gases from water is eliminated.

3. Since for these fuel-nitrogen studies gas phase analyses are essential, elimination of the water quench assures higher accuracy by reducing possible gas losses due to solution in the excess water. Dilution of the effluent gases does, however, become a potential problem at very low concentrations.

Nitrogen, argon, and helium have been tested for efficiency of quenching. Argon has been found to cool the hot main gases most efficiently. Typical gas quench flow rates required are about 25 ℓ/min with a main gas flow rate through the collector of 3 ℓ/min. (corrected to room temperature), which is half of the total main gas flow rate supplied to the furnace of 6 ℓ/min.

The reason the gas quench is feasible in the present system is that the quantity of hot main gas removed through the collector is much smaller than that in the system descibed in Section III-1.1.0 (3 ℓ/min. versus 30 ℓ/min,).

III-2.2.2 GAS PREHEATER

The main gas enters the furnace through the top plate at room temperature. Heat transfer calculations show that at any furnace temperature and the maximum gas flow rate of 6 ℓ/min. (measured at room temperature), the gas reaches the furnace temperature before leaving the alumina honeycomb. These predictions are confirmed by measuring the gas temperature with a Pt-Rh thermocouple as it passes through the honeycomb. The system has nevertheless been equipped with a packed bed preheater for use with higher gas flow rates. The preheater is placed upstream of the furnace main gas inlet and consists of a Lindberg model 55081-A tubular heater (120 V,8.5 A) capable of reaching a temperature of 1000°C. The packed bed, made of about 5 mm. alumina pellets, is 12 inches in depth and is contained in a 1 inch O.D. stainless steel tube.

III-2.2.3 VACUUM SYSTEM

Suction for the drawing of gases through the collector probe is accomplished by the use of two Cenco Megavac pumps in parallel. These pumps (115 V, 6 A, 1/3 hp) have individual capacities of 57 ℓ/min. maximum at 1 atmosphere. The vacuum flow rate is simply controlled by a regulating valve. All vacuum lines are 1/2 inch in diameter or larger to help minimize pressure drops and maximize pumping speeds.

III-2.2.4 PREPARATION OF CHAR

In selecting a char for the oxidation and kinetics studies, two criteria must be satisfied. First, the char should contain a minimum of volatiles (largely carbon and hydrogen) at the temperatures and residence times pertinent to the oxidation experiments. A volatile-free char would permit isolating the contributions of purely heterogeneous processes in the study of fuel nitrogen conversion to nitric oxide. Second, the char should retain as large a percentage as possible of the nitrogen originally present in the coal so that the fate of the char-nitrogen during oxidation can be accurately studied with a minimum sampling error. Taking into account both criteria, the char used for this study was produced by pyrolyzing lignite coal particles at 1750°K for a residence time of one second. The char produced was then size-graded to select particles in the 38 to 44 micron size range for further oxidation experiments. For the production of char, a minor modification is made to the furnace in free-fall mode (Section III-2.1.0) in order to permit the collection of the char in a holding flask.

III-2.2.5 EXPERIMENTAL PROCEDURE

The furnace is heated at 250 to 350°C per hour to the desired temperature by using the automatic temperature controller and programmer. The final temperature is checked with the platinum-rhodium thermocouple extending just below the honeycomb. Typical temperature profiles along the muffle tube axis are determined by moving a platinum-rhodium thermocouple along the axis from the bottom of the furnace. Once the furnace has reached the desired temperature, a preweighed bronze filter is placed in the collector probe. About 1 gram of char is weighed and placed in the feeder with the needle valve closed. The quenching gas flow rate and vacuum are set to just counter each other at about 25 ℓ/min. so that the furnace pressure does not change rapidly as the probe is put into the muffle tube. The collector is then raised into the furnace and secured at a particular height. An O-ring, through which the probe is pushed, seals the muffle tube from the external atmosphere. The main gas is next adjusted to provide the desired oxidizing gas partial pressure using helium as a diluent. The total main gas flow rate is always 6 ℓ/min. STP with a maximum of 3 ℓ/min. being drawn into the collector for purposes of proper quenching. The remainder of the gas passes out the bottom of the furnace, its flow rate being controlled by a rotameter in conjunction with the vacuum control valve. As the main gas is being set, the furnace pressure is continuously monitored and maintained at a slight positive pressure (less than 1 psig), also by adjustment of the vacuum. Once the muffle tube has been purged for 2 min., the carrier gas is set at about 30 cc/min. (only 1/2 of 1 percent of total main gas flow) and the needle valve and vibrator are adjusted so that the char feeds fairly consistently in 6-7 min. or at a rate of about 0.15 g/min. When the feeding is finished, the main gas is turned off and the collector probe is removed. The quenching gas and vacuum are then turned off and the filter is very quickly removed and weighed to avoid adsorption of moisture. Finally, the samples are stored in sealed glass vials to await further analyses.

III-3 PROCEDURES FOR MEASURING NITRIC OXIDE REDUCTION BY CHAR

The NO-char experiments are carried out in the alumina muffle tube furnace operated in the free-fall mode as described in Section III-2.1.0. Mixtures of nitric oxides in helium (or argon), supplied by Matheson Gas Company, are used as main gases. Three different concentrations of nitric oxides, i.e. 530 ppm and 6,400 ppm (all balanced in Helium) and 1100 ppm (balanced in Argon), have been used. The char used in this study was prepared by the procedures described in Section III-2.2.4. The main gas flow is typically on the order of 3 ℓ/min. A Chemiluminescent NO-NO_x Gas Analyzer and a chart recorder are used to monitor the NO concentration in the furnace exit stream (See Section III-4). Two to three minutes after the NO containing stream is first introduced into the furnace, the NO concentration in the exit stream stabilizes at the concentration of the inlet stream. After steady conditions have been reached, char feeding is commenced and the decrease in NO concentration in the exit stream is observed and recorded continuously. After completion of the char feeding, the NO concentration in the exit stream returns gradually to its original level. When the NO concentration in the exit stream has returned to its original level and stabilized, the main NO gas is turned off and a secondary helium gas is introduced into the furnace to purge the furnace until no more NO can be detected. The secondary helium gas is then turned off and the residue char is removed from the sintered bronze disc filter for analysis.

III-4.0 GAS PHASE ANALYSES

Analysis of the volatile pyrolysis and oxidation products formed in the furnace complements the weight loss data obtained through analysis of the char. Emphasis was placed here on analysis for nitrogen-bearing species, especially NO, HCN, and NH_3, though some efforts were made to detect N_2 by gas chromatography. Carbon containing species of interest included CO, CO_2, and CH_4, analysis for higher hydrocarbons being outside the scope of this work. In all cases, volatile products passed through the furnace hot zone, obscuring any distinction between primary and secondary products. Methods employed for analysis are detailed below.

III-4.1 CHEMILUMINESCENT GAS ANALYSIS OF NO_x

A Thermo Electron Model 10B Chemiluminescent NO-NO_x Gas Analyzer is used for the analysis of NO_x. Combustion gases are withdrawn continuously from the furnace, passed through a filter to remove soot and tar, then fed into the analyzer for NO_x analysis. This instrument has a typical response time of 1.7 seconds and an operating range of 2.5 to 10,000 ppm. The meter response to NO_x is recorded on a strip chart recorder and integrated over time. This technique allows the fraction of the nitrogen in the coal that is converted to nitrogen oxides to be determined. Any nitrogen dioxide present is converted to nitric oxide by a molybdenum converter prior to nitric oxide detection. The chemiluminescence meter is calibrated at the operating conditions used during actual sampling by using nitrogen gas as a zero gas and a series of certified nitrogen oxide in helium calibration gases supplied by Matheson Gas Company. The concentrations of calibration gases are confirmed by independent Saltzman analysis for the total nitrogen oxides in accordance with ASTM procedures.

III-4.2 COLORIMETRIC ANALYSIS OF NH_3

The basic gas sampling unit consists of two bubblers, a flow regulator, and a wet test meter. Off-gases from the furnace are passed through the bubblers containing 0.1 N H_2SO_4 solution to absorb NH_3. A sample aliquot from the bubbler is then tested for ammonia content by the direct Nesslerization method in accordance with ASTM procedures.

III-4.3 STANDARD SPECIFIC ION ELECTRODE ANALYSIS OF HCN

HCN gas from the furnace exit stream is collected in a gas sampling unit. The gas sampling unit is essentially identical to the unit used for NH_3 sampling except that the absorbing agent in the bubblers is now changed to 0.1 N NaOH solution. After absorption has been completed, an aliquot of 0.01 N $Pb(NO_3)_2$ is added to the sample solution for the removal of the potential interference by S^{--} ion derived from the coal surface. The cyanide content in the sample solution is then measured by an Orion cyanide ion electrode model 94-06. The electrode is calibrated frequently against a series of standard NaCN solutions which are prepared daily.

III-4.4 GAS CHROMATOGRAPHIC ANALYSIS OF N_2, CO, CO_2, and CH_4

Calibrated Instruments' five-layer material gas sampling bags are used to collect gases from the furnace exit streams. The sampling bag is then connected to a gas chromatographic system and gases are introduced into a sample loop for GC analyses. The GC system is a Fisher/Hamilton Model 29 Gas Partitioner. This instrument is equipped with two columns. Column Number One is packed with 30% Di-2-ethylhexylsebacate on 60-80 mesh Chromosorb P and Column Number Two is packed with 40∿60 mesh Molecular Sieve 5A. Both columns are operated at room temperature. Alternatively, the packing materials in both columns can be simultaneously replaced by Porapak Q with Column Number One operating at room temperature and Column Number Two operating at dry ice temperature (-78°C). The chromatograph is calibrated against a standard gas before and after each sample run to ensure accuracy. The standard gas, supplied by Matheson Gas Company, consists of known concentrations of CO, CO_2, CH_4, N_2, and H_2 in Helium. Total CO, CO_2, CH_4, and N_2 emissions from the furnace are calculated by normalizing the GC signals to those of the standard gases.

III-4.5 NON-DISPERSIVE INFRARED ANALYSIS OF CO AND CO_2

Co and CO_2 from the furnace are also measured by Beckman Non-Dispersive Infrared Analyzers. Model 315A is used for CO_2 analysis and Model 315B for CO. Gases from the furnace exit stream are introduced directly into thses instruments for a continuous monitoring of CO and CO_2. The instruments are calibrated frequently against standard CO and CO_2 mixtures respectively.

III-5 ASTM PROXIMATE EQUIPEMENT

A drying oven, a cylindrical furnace, and a brick-insulated furnace are used to determine moisture, volatile matter, and ash contents. ASTM standards (D3173-73, D3174-73, and D3175-73, 1972) are followed wherever possible. Some modifications are made, however, to accommodate smaller sample sizes and different experimental equipment. A Hoskin cylindrical furnace (Model 303, 5.0 amps) is the main part of the system to determine volatile matter. The furnace is capable of a maximum temperature of 1100°C at full load. The heated cylindrical tube is 1.38 inches in diameter and 13 inches long. The equipment has a cooling section 15 inches long and 1.5 inches I.D. in order to provide adequate cooling for the devolatilized samples in an inert atmosphere. This prevents oxidation of the hot samples. The whole assembly is sealed with a high temperature alumina cement. The furnace is continuously purged with nitrogen when determining proximate volatile matter. A chromel-alumel thermocouple is centered in the heating zone 5.0 inches from the bottom. A porcelain crucible (5 mℓ capacity) containing the samples to be analyzed is suspended in the hot zone of the furnace about 0.2 inches above the tip of the thermocouple. A reasonably steady hot zone (± 20°C) is maintained 4.3 inches to 8.6 inches from the bottom.

Volatile matter determined by this system has been compared with the results of two independent laboratories (Galbraith Laboratories, Inc., Knoxville, Tennessee and M.I.T. Central Analytical Facility) which followed the ASTM specifications. Agreements within

0.5 percent of the weights of original coals were obtained. The agreement justifies the present system.

Ash content is determined in a magnesium brick furnace. The inside dimensions of the furnace are a base 8.5 inches by 4 inches and a height of 9 inches. This furnace is large enough to accomodate the cylindrical alumina collector used in the free-fall experiment. Four silicon carbide heating elements (Norton XL 3/8 in. O.D. by 13 inches long) supply necessary heat to the furnace. Glazed porcelain crucibles are used to hold the samples. It was confirmed that the use of different crucible sizes did not affect ash content. ASTM standard procedures were used with the exception of the size of the crucibles and samples.

SECTION IV

COAL CHARACTERIZATION

Coals differ widely depending on geological age, geographical location and geological conditions. Major differences may be found in coal composition even between different positions in a particular coal seam. Classifications developed to differentiate between different coals have been based on rank, physical appearance, elemental analysis, and functional group analysis.

Rank is a gross measure of properties such as heat of combustion, carbon content, agglomerating and aggluting tendencies of coals with definitions differing between countries.

Because of ease of utilization, rank, sometimes supplemented by elemental analysis, has been the classification adopted by industry for providing a measure of those properties that determine the end use of coal. Research workers have been seeking a more fundamental measure of coal behavior and limited success has been achieved using petrographic analysis. Functional form analysis provides a more fundamental measure of coal structure but its use is qualified by the difficulty of the measurements, which usually require solvation of the coal with possible modification of the coal structure.

It is a long-range objective of fundamental coal studies to correlate the behavior of coals with a classification scheme,

IV-1.0 MONTANA LIGNITE

The Montana lignite was chosen as representative of a low rank, low sulfur, non-caking western coal which could be strip mined. These coals are likely to find future use as raw material for gasifiers and possibly as fuel for local power generation. The reserves of lignites in the United States represent approximately 6×10^4 quadrillion BTUs or 28.8% of the ultimate United States Coal reserves.

preferably simple. For the current study, a lignite and a bituminous coal, two widely different coals, have been selected. The characterization of these is given below.

IV-1.1 VISUAL APPEARANCE OF MONTANA LIGNITE

Scanning electron micrographs of the Montana lignite used in these studies are shown in Figure IV-1. The lignite has been ground and classified to nominally 38-43 microns. The low magnification micrograph shows many small particles have escaped mechanical size classification and a few large, irregularly shaped particles are also present in the supposed narrowly-sized fraction. The micrographs at higher magnification show the particle surface is relatively smooth, has few visible macropores, and has ash particles on the order of several microns physically held on the surface.

The photomicrographs of polished sections under oil immersion are shown in Figure IV-2. The micrographs show that the coal particles are not uniform in internal macropore area or in reflectance. Four different levels of reflectance have been identified in the polished section slides. Most particles appeared to be composed of only one petrographic element although occasionally one particle will contain as many as three different elements.

The top micrograph in Figure IV-2 shows three particles of different reflectances. The whitish particle on the right side of the micrograph is tentatively identified as micronite; the highly reflective fusanite particles are very rare in lignites and are not evident in the samples; the dull, barely visible particle just to the left of the micronite particle has been identified as exinite; and the particle below and to the left of the exinite particle has been identified as vitrinite. The top micrograph shows some macropore structure in the vitrinite and exinite, but most of the

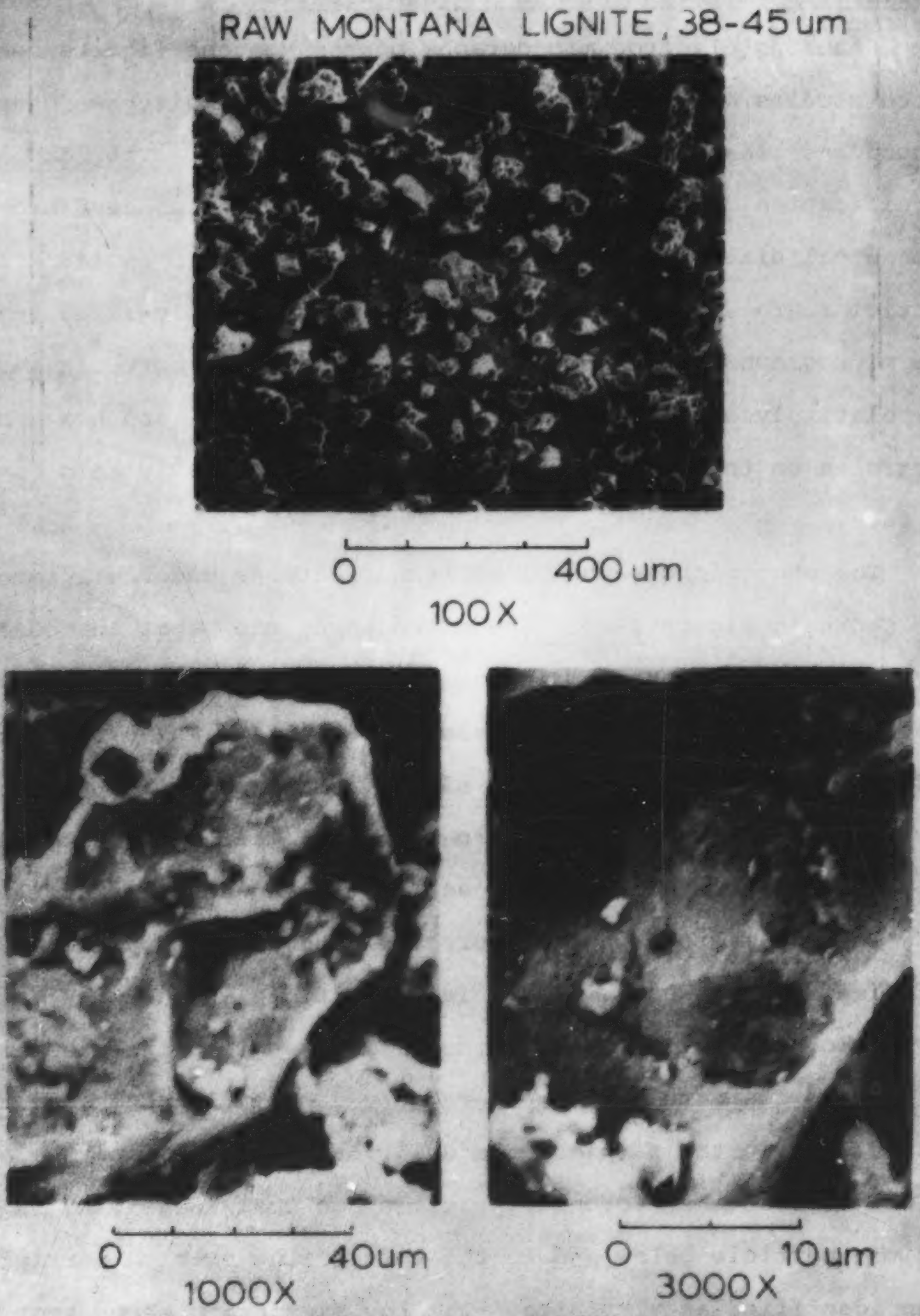

RAW MONTANA LIGNITE, 38-45um
0
400 um
100 X
0
40um
1000X
0
10um
3000X

FIGURE VI-1. Scanning electron micrograph of raw Montana lignite-A.

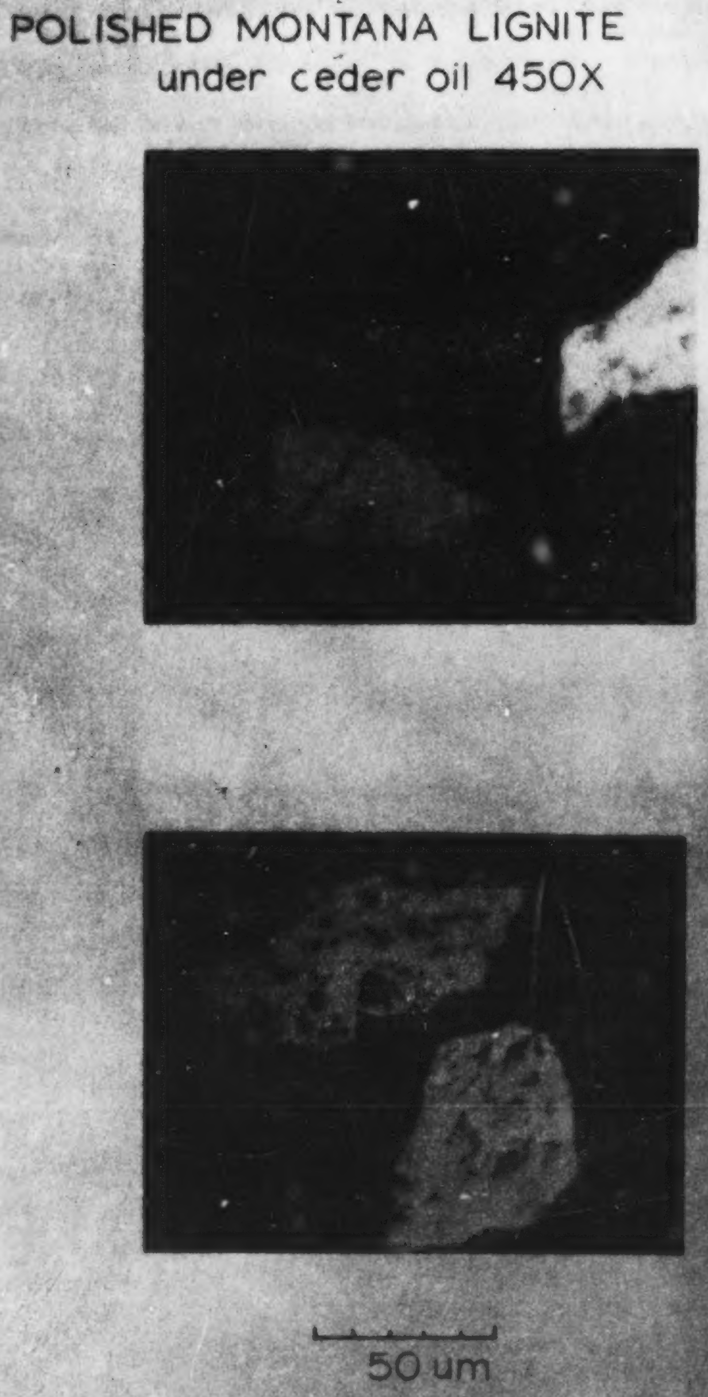

POLISHED MONTANA LIGNITE
under ceder oil 450X
50 um

FIGURE VI-2. Photomicrograph of polished raw lignite-A.

macropore structure is in the medium reflective micronite. The macropores appear either in micronite in the form of circular voids as large as ten microns in diameter or as dentritic-like structures with stem diameters on the order of several microns. Fewer pores are visible in vitrinite and exinite; these pores are either irregular shaped voids on the order of 5-10 microns in diameter, or relatively straight fissures, about one micron in diameter.

IV-1.2 PARTICLE SIZE DISTRIBUTION

The Montana lignite was received as 1/8 inch particles. These particles were ground in a ball mill and separated through roto-tapped Tyler screens. Most of this study was conducted with the 38-43 micron size range, although some data was taken using the 74-88 micron size range. These two size ranges were chosen as being representative of coal fed to a pulverized coal flame.

The electron micrograph in Figure IV-1 showed that the closely sized fraction had a number of undersized particles and a few oversized particles, shown more quantitatively by the particle size distribution in Figures IV-3 and IV-4. The cumulative mass distribution was fitted with the Rossin-Rammler (1939) distribution function, as for example in Figure IV-3. Scanning electron micrographs of lignite particles were counted on a Zeiss particle counter and Rosin-Rammler parameters were developed using a least square fit of the particle frequency. The mean particle diameter derived from the Rosin-Rammler distribution was 52.3 microns. The Rosin-Rammler derived curve is compared in Figure IV-4 with the original data. The original data gave a mean particle size distribution of 47.6 microns and a standard deviation of 15.2 microns. The fit of the data is considered satisfactory, in spite of the differences in calculated and measured frequency at large particle diameters, because the size interval is small and relatively few oversized particles are present.

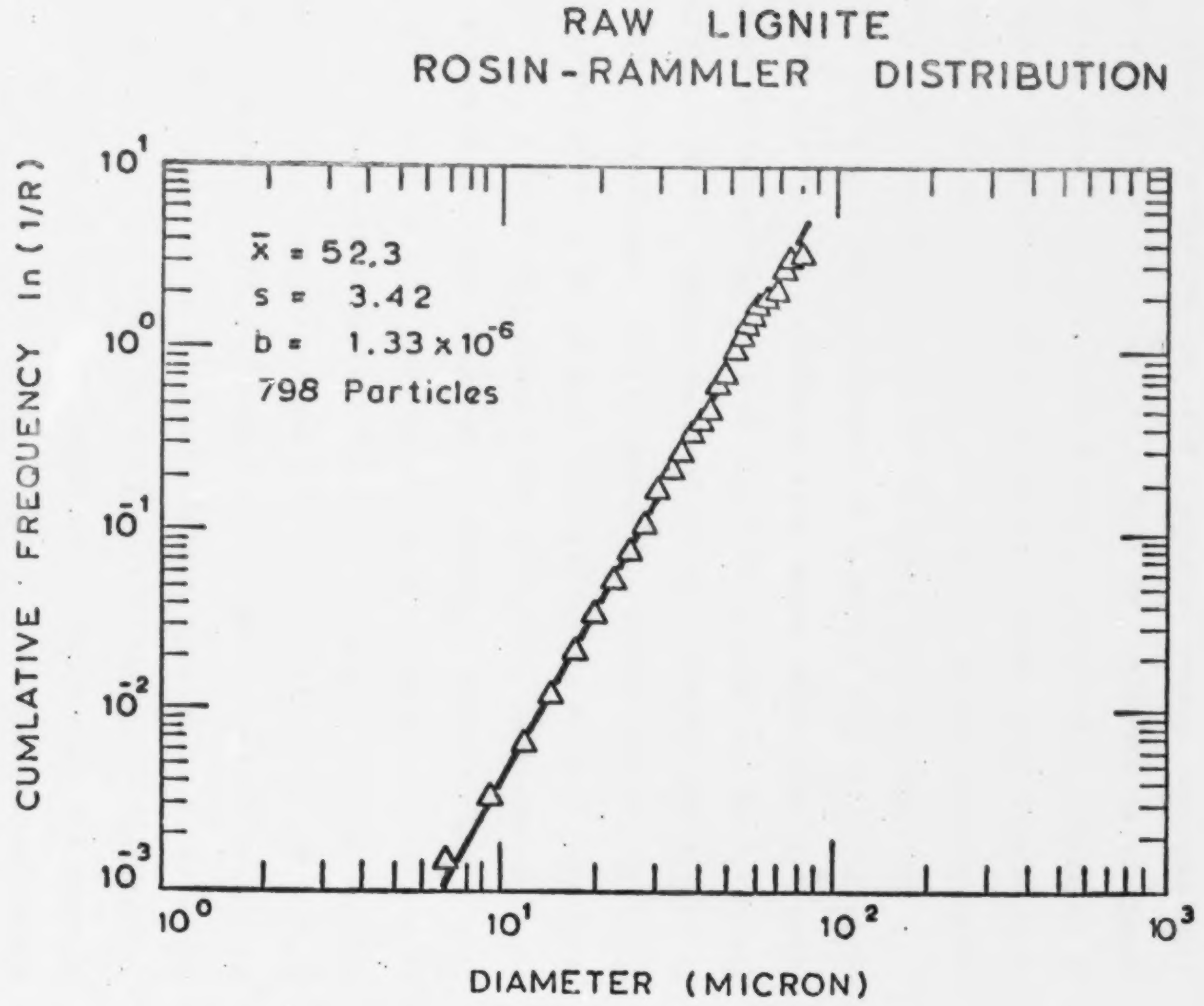


FIGURE IV-3. Rosin-Rammler accumulative size distribution of lignite particles

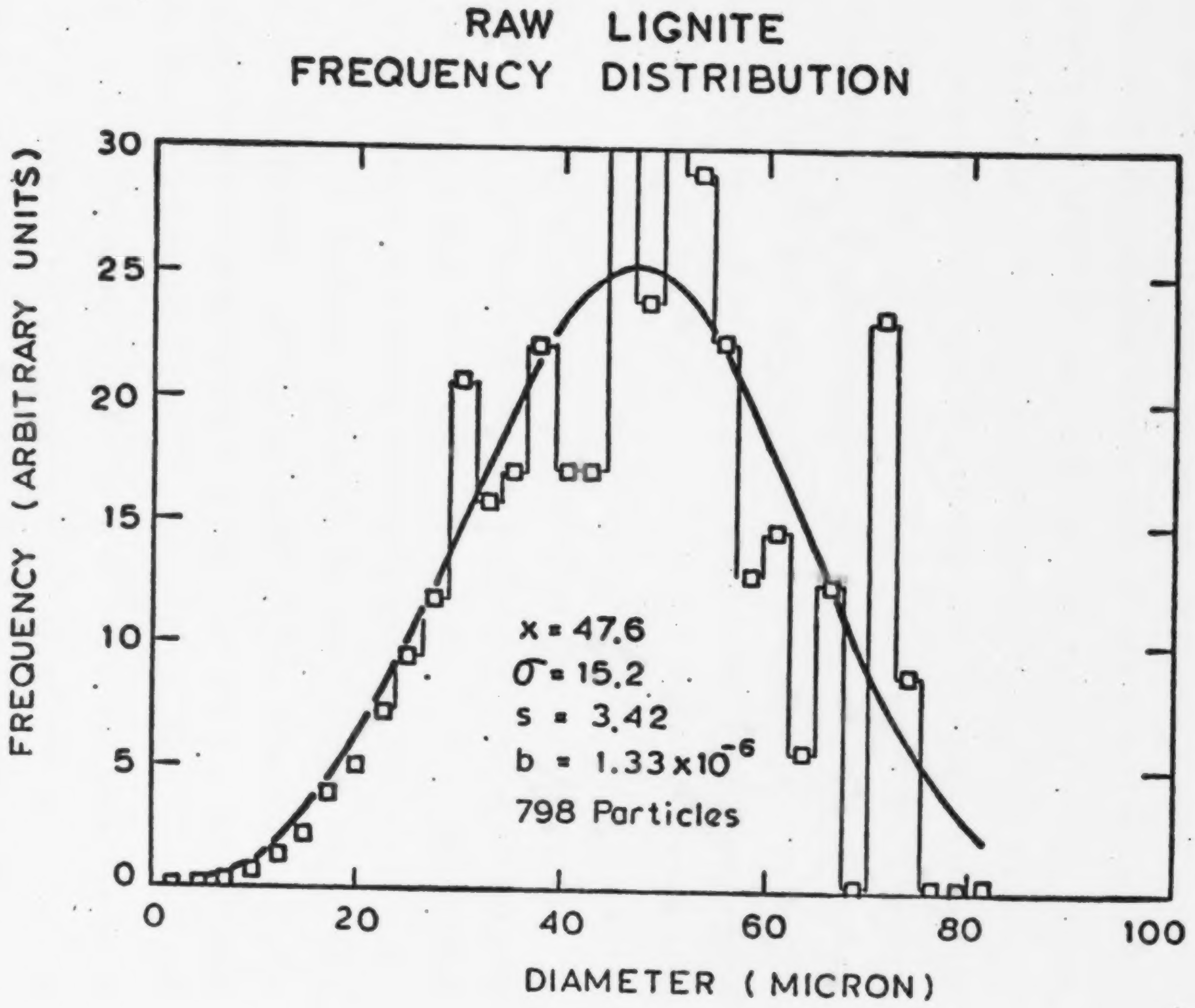


FIGURE IV-4. Lignite particle size frequency distribution.

IV-1.3 SURFACE AREA

Numerous measurements of surface areas of raw coal and processed coals have been reported. Spencer and Bond (1966), however, have questioned the use of adsorption isotherms to derive absolute surface areas of microporous solids. Van Krevelen (1961) showed that the areas determined by conventional adsorption methods at liquid nitrogen temperatures are two orders of magnitude lower than values derived from adsorption at room temperature or values derived from methanol heat of wetting data. The diffusion process appears to have an activation energy of about 4 kcal/gmole. The activated diffusion process accounts for the low values of surface area obtained at low temperature, because the adsorbate cannot penetrate completely into the microstructure of coal in a reasonable period of time at low temperatures.

Marsh (1965) has reviewed the various methods of determining surface area and concluded that adsorption of CO_2 near room temperature gives the most reasonable values for surface areas of coal and cokes. Typical surface areas for coals with less than 85% carbon (dmmf) are in the range of 200 m^2/g. Adsorption of inert gases at 77°K gives values on the order of 2 m^2/g. Adsorption of krypton at 77°K for the lignite used in this study gave a surface area of 2 m^2/g when analyzed using the Dubinin-Polanyi equation and 1.2 m^2/g when analyzed using the BET equation. These values are not representative of the total surface area but are considered to be representative of that fraction of the surface area contained in pores with diameters greater than about 12 A. (See Van Krevelen, Marsh, Gan, et al, 1972, and Tingey and Morrey, 1973).

Surface areas from CO_2 adsorption at room temperature have not been measured for the coals used in this study. The surface area is expected to be reasonably close to the surface area of 183 m^2/g measured by Nsakala et al (1975) for a North Dakota lignite with a daf carbon content of 71%. THis value is slightly lower but in reasonable agreement with the surface areas found by Gan et al (1972) of 225-308 m^2/g for North American lignites containing between 63 and 72% carbon. Swann et al (1974) report a value for the CO_2 adsorption area of Australian Yallourn brown coal of 290 m^2/g comparable to that of American lignites.

The integrated particle size distribution curve yields a superficial surface area of 0.11 m^2/g. This value is 20 times smaller than the krypton adsorption area and 2000 times smaller than the normal CO_2 areas for lignites.

IV-1.4 PROXIMATE ANALYSIS

Proximate analysis- moisture, volatile matter, and ash content- were performed at three independent laboratories with similar results. The proximate analyses are reported in Table IV-1 along with other information for the two coals used in this study. The volatile matter was approximately 36.2%, the equilibrium moisture content was close to 13.6%, and the ash was 7.8% on an as received basis. The lignite was treated as a sparking coal.

TABLE IV-1

COAL CHARACTERIZATIONS

COAL	MINE	BTU/lb MOIST MM FREE*	PROXIMATE ANALYSIS A.R. Wt. %			ULTIMATE ANALYSIS A.R. Wt. %					SULFUR FORMS		
			H_2O	VM	ASH	C	H	N	S	By Diff. O	Pyr-itic S	SO_4	Organic S
PITTSBURGH SEAM #8 hvA-b	IRELAND	14,377	2.2	40.7	10.8	67.81	5.03	1.20	4.83	8.55	2.50	0.69	1.62
MONTANA LIGNITE-A	SAVAGE	8,809	13.6	36.2	7.8	54.50	4.96	0.88	0.84	17.14	0.11	0.18	0.55

* HIGHER HEATING VALUES WERE CALCULATED ON THE BASIS OF EQUILIBRIUM MOISTURE WITH MINERAL MATTER, AS DETERMINED BY PADIA (1976) FROM LOW TEMPERATURE ASHING, REMOVED. THE MINE MOUTH MOISTURE CONTENT OF THE BITUMINOUS COAL WILL BE CLOSE TO ITS EQUILIBRIUM MOISTURE CONTENT SO THE HEATING VALUE WILL REMAIN UNCHANGED. LIGNITE FROM THE SAVAGE MINE HAS BEEN FOUND BY PAULSON ET AL. (1972) TO CONTAIN 28.2% MOISTURE; THE HEATING VALUE CALCULATED ON THIS BASIS WOULD BE 7346 BTU/lb.

IV-1.5 HEAT OF COMBUSTION

Rank classification of coal, below 69% daf carbon content, is based on the heating value and the agglomerating and aggluting properties of the coal. The heating value is the high heating value of the coal (water as a liquid) on moist mineral free basis. The mineral matter is usually calculated based on the ash and sulfur content of the coal by empirical equations, most frequently the Parr formula, but is best obtained by use of low-temperature ashing.

The heat of combustion was measured on a dry sample of the Montana lignite and corrected to a moist mineral free basis using the mineral matter determined by low temperature ashing and either the equilibrium moisture content or the moisture content found by Paulson et al (1972), for samples from the same mine. The heating values are in reasonable agreement with heating values previously calculated using the Dulong formula. The measured heating value is reported in Table IV-1 as 8809 BTU/lb with equilibrium moisture content and 7346 BTU/lb with mine moisture; the latter value classifies the coal used in this study as lignite-A.

IV-1.6 ELEMENTAL ANALYSIS

Ultimate analysis of the coals used in this study were performed at the Galbraith Laboratories, Inc., Knoxville, Tennessee and are reported in Table IV-1 on an as received basis and in Table IV-2 on several common bases. Sulfur form analysis is also reported in Table IV-1.

The Montana lignite contained 73.3% carbon on a dry mineral matter free basis, 0.83% nitrogen and 0.98% sulfur on a dry basis. Approximately 65% of the sulfur is organic sulfur. Oxygen was determined by difference and is not considered very accurate. Oxygen is determined by substracting ash and all other elements from 100%. This procedure can lead to rather substantial errors in the oxygen concentration because mineral matter changes weight when sulfides and carbonates react during ashing. The procedure gives 22% too high an oxygen concentration for the Montana lignite.

TABLE IV-2

LIGNITE

CHARACTERIZATION OF MONTANA LIGNITE
FROM THE SAVAGE MINE IN RICHLAND COUNTY,
GROUND AND CLASSIFIED TO 38-45μ

COMPONENT	ULTIMATE AIR	ULTIMATE DRY	ULTIMATE daf	ULTIMATE dmf*	ULTIMATE C-H-O BASIS
H_2O	13.60	-	-	-	-
C	54.90	63.54	69.88	73.30	71.30
H	4.96	5.74	6.31	6.62	6.44
N	0.72	0.83	0.92	1.23	-
Pyritic S	0.11	0.13	-	-	-
SO_4	0.18	0.21	-	-	-
ORGANIC S	0.55	0.64	0.73	0.73	-
TOTAL S	0.84	0.98	-	-	-
ASH	7.84	9.07	-	-	-
O(DIFF.)	17.14	19.84	22.16	18.12	22.26

* MINERAL MATTER FOUND FROM LOW TEMPERATURE ASHING BY PADIA (1976) TO BE 11.50% (WET BASIS)

IV-1.7 ASH ANALYSIS

The mineral elements of ash (Table IV-3) were determined by atomic absorption of the metallic elements, reported as if the elements are in their natural oxidation state.

The principal component of mineral matter in coals is common clay such as SiO_2 and Al_2O_3. The ash from a Montana lignite contained 27% silica and 16% alumina. The ash also had high concentrations of calcium (28% as CaO), magnesium (9% as MgO), and a surprisingly large amount of sulfur (13.5% as SO_3). Iron and phosphors are the only other significant elements; Fe_2O_3 accounts for 3.4% of the ash and P_2O_5 accounts for 1%. Titanium, potassium, and sodium are the remaining major elements in the lignite ash.

TABLE IV-3

ASH CHARACTERIZATION*

Wt.% on ignited basis	Montana Lignite-A	Pittsburgh Seam #8 High Volatile Bituminous-A
Ash	7.84	10.55
P_2O_5	1.02	0.30
SiO_2	26.80	37.52
Fe_2O_3	3.41	29.34
Al_2O_3	16.41	19.15
TiO_2	0.50	0.57
CaO	28.44	4.65
MgO	9.02	0.73
SO_3	13.45	4.10
K_2O	0.35	1.29
Na_2O	0.27	0.38

* Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee and Padia (1976).

IV-1.8 FUNCTIONAL GROUP ANALYSIS

No functional group analysis has, as yet, been performed on the coals used in this study, nor has a functional group analysis of the lignite used in this study been found in the literature. Tingey and Morrey have compiled average functional group analyses for various rank coals from literature values. Values for the functional group composition for a lignite of 70.6% carbon will be used for comparison purposes until direct measurements become available.

Tingey and Morrey's functional group distribution is shown in Table IV-4. A lignite can be expected to have an average ring size of about 2-4, 27% of the carbon will be aliphatic carbon and 65% of the hydrogen will be attached to aliphatic carbons. Most of the carbon (51.7%) in such small ring systems is peripheral carbon. The aliphatic hydrogen is mostly attached to aliphatic carbon that is attached either to α or β position to an aromatic ring; hydroxyl hydrogen accounts for only 4.6% of the hydrogen.

Oxygen concentration and distribution are not included in the functional group summary presented by Tingey and Morrey. Oxygen concentrations can be estimated by difference, after allowance for a concentration of nitrogen and sulfur of about 2%. The oxygen concentration obtained by difference is 23%, which is a high but reasonable value for an American lignite. Hydroxyl oxygen may then account for a third of the oxygen present with most of the remaining oxygen present as carbonyl oxygen. These results are consistent with generalized analysis reported by Dryden (1963).

TABLE IV-4

FUNCTIONAL GROUP ANALYSIS OF A LIGNITE

From Tingey and Morrey (1973)
and Dryden (1963)

	Hydrogen Distribution % of total H	Carbon Distribution % of total C	Oxygen Distribution % of total O
Total daf	4.74	70.6	~22.
Average Ring Sizes	-	2-4	-
Aromatic	30.7	73.2	-
Monoring	16.4	13.2	-
Condensed Ring	14.3	11.5	-
Peripheral C	-	51.7	-
Interior C	-	21.5	-
Aliphatic	64.7	26.8	-
Methylene Bridges	14.0	16.9	-
α CH_x	25.7	17.6	-
β CH_x	23.7	9.2	-
Hydroxyl	4.6	3.7	~36.
Carbonyl	-	-	~45.
Carboxyl	-	-	~19.

IV-2.0 PITTSBURGH SEAM #8 BITUMINOUS COAL

The Pittsburgh bituminous coal was chosen as a coal representative of a deep mined, high sulfur, caking eastern coal. This coal is highly swelling and caking and is representative of coals that might be used in coking operations or in direct fired utility boilers. United States reserves of bituminous coal represent about 46% of total coal reserves or approximately 9.6×10^4 quadrillion BTUs.

IV-2.1 VISUAL APPEARANCE OF PITTSBURGH BITUMINOUS COAL

The bituminous coal was ground and classified in the same manner as the lignite. Scanning electron micrographs of the classified bituminous coal are shown in Figure IV-5. The electron micrograph at low magnification shows, as for lignite, irregular shaped particles and poor classification. There are more fines present in the bituminous coal than in the lignite, and this is thought to be because the bituminous coal has much lower equilibrium moisture content and exhibits more pronounced static attraction. The bituminous coal, when viewed under higher magnification, appears to have a hard, smooth surface with some visible fracture patterns. The lignite had very few macropores but the bituminous coal appears to be almost entirely free of such large external openings. A few micron-size ash particles were observed clinging to the bituminous coal particle surface.

Polished surfaces of bituminous coal, shown in Figure IV-6, viewed under cedar oil exhibit similar petrographic elements to those observed earlier for lignite. The predominance of a low reflecting element, most likely vitrinite, and two elements that reflect more light are seen in the top micrograph. The larger and darker of the two highly reflecting elements appears similar to the element identified as micronite in the lignite; the smaller highly reflective element appears to be a rare fusanite element. The macropore structure of the micronite elements appears to be less pronounced than was found for the lignite, but the lower reflective elements in bituminous coal appear to have greater macropore

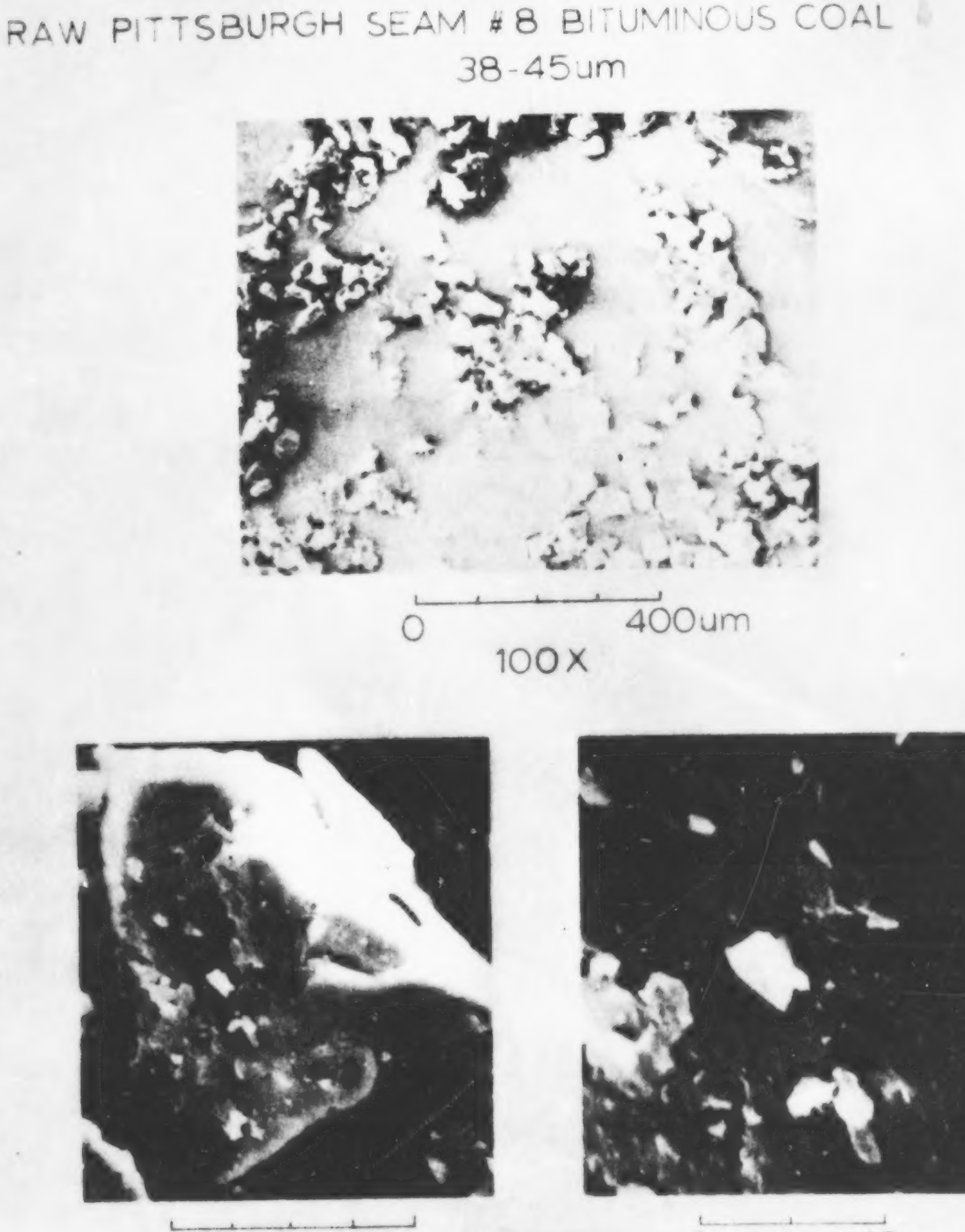

RAW PITTSBURGH SEAM #8 BITUMINOUS COAL
38-45um
0
400um
100X
0
40um
1000X
0
10um
3000X

FIGURE VI-5. Scanning electron micrograph of raw Pittsburgh seam #8 hvA bituminous coal.

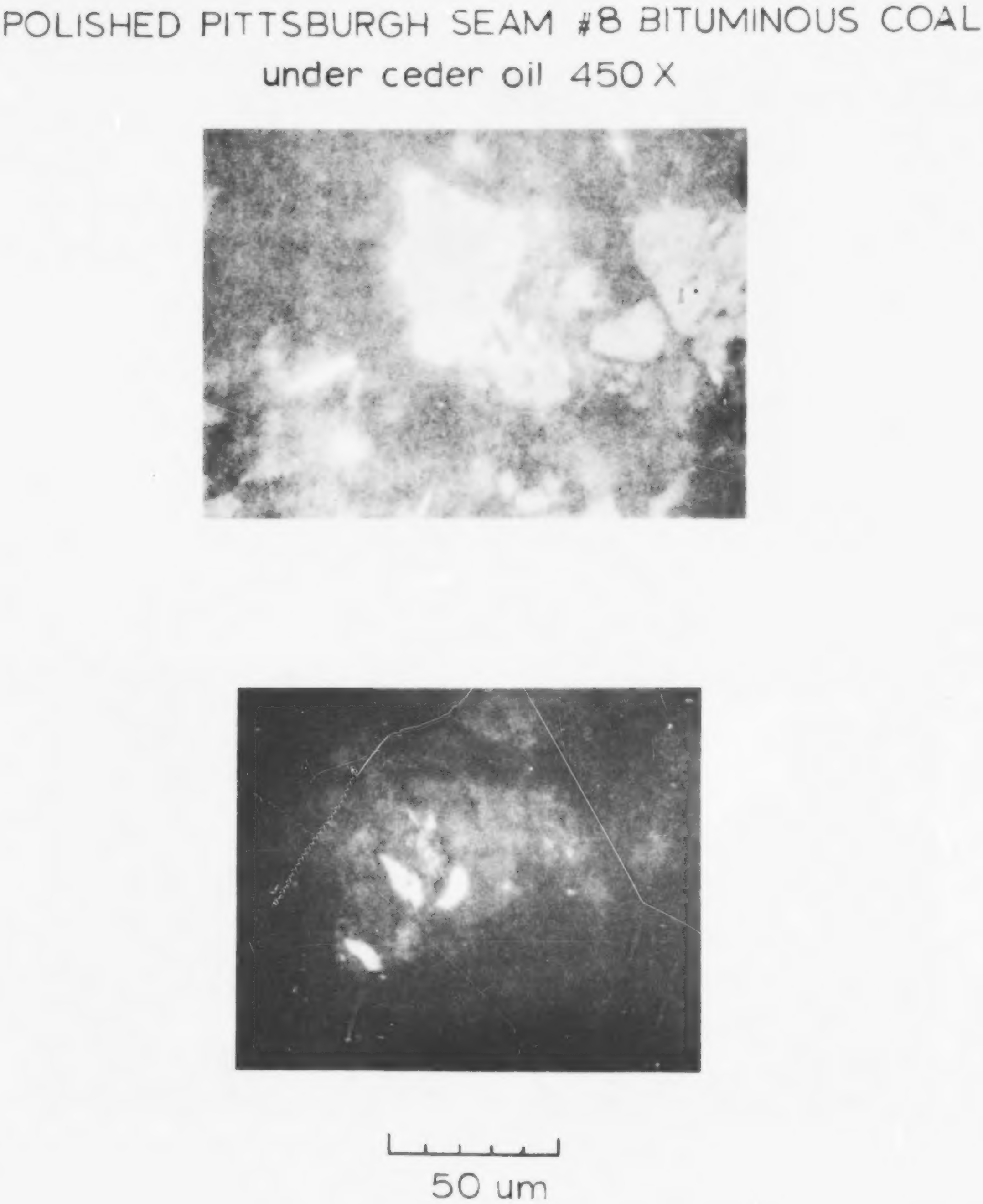

POLISHED PITTSBURGH SEAM #8 BITUMINOUS COAL
under ceder oil 450X
50 um

FIGURE VI-6. Photomicrograph of polished raw Pittsburgh seam #8 hvA bituminous coal.

structure than the lignite. As in the lignite, most particles are petrographically pure, although several petrographic forms are occasionally observed; for example, three different reflectivities are evident in one particle in the bottom micrograph.

IV-2.2 PARTICLE SIZE DISTRIBUTION

Mass particle size distribution, calculated in the same manner as for the lignite gave a poorer fit of the data for bituminous coal than for lignite, even though more than three times as many particles were counted. The fit of cumulative particle mass by the Rosin-Rammler distribution function is shown in Figure IV-7. The mass average particle size determined from the cumulative distribution is 64.9 microns, while average particle diameter determined from the raw data is 57.5 microns and the standard deviation is 22.2 microns. The average particle size determined from both methods is larger than the maximum screen size of 43 microns. A 43 micron opening could allow a particle with a maximum dimension in at least one direction of about 60 microns to pass. Narrow particles with two dimensions less than the maximum size opening could pass through the screen with a very large size in one dimension. Electron micrographs were checked and a few odd shaped particles appeared in the pictures. A few large particles can skew a mass average distribution to much higher mass average particle sizes. Another possibility that cannot be completely eliminated, but which could account for the large particles present in the classified sample is rents or enlarged holes in the screens. The original data and the derived Rosin-Rammler distribution curve are shown in Figure IV-8. The agreement is considered satisfactory with the reservations previously mentioned in the section on lignite distribution.

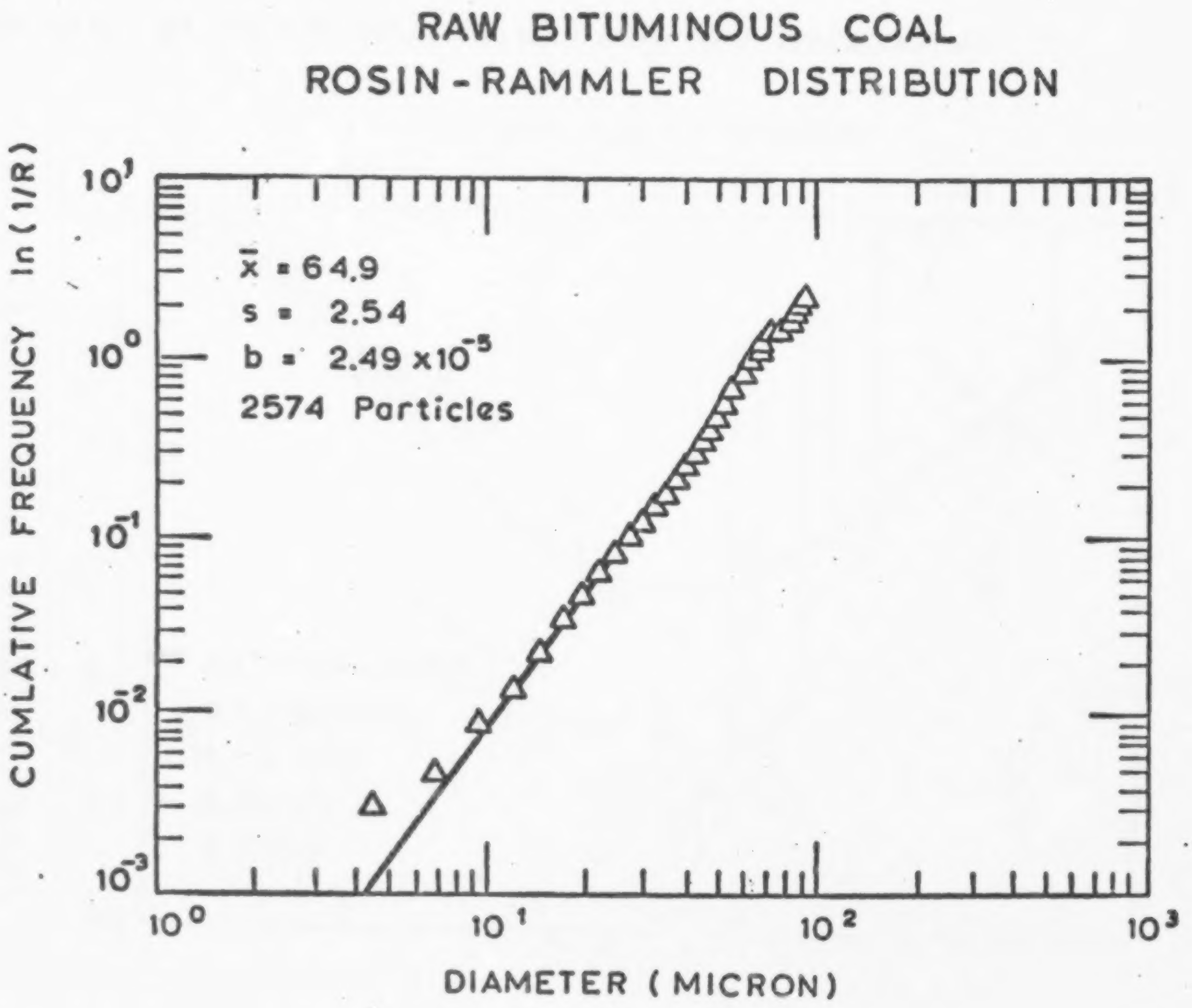


FIGURE IV-7. Rosin-Rammler accumulative size distribution of bituminous coal particles.

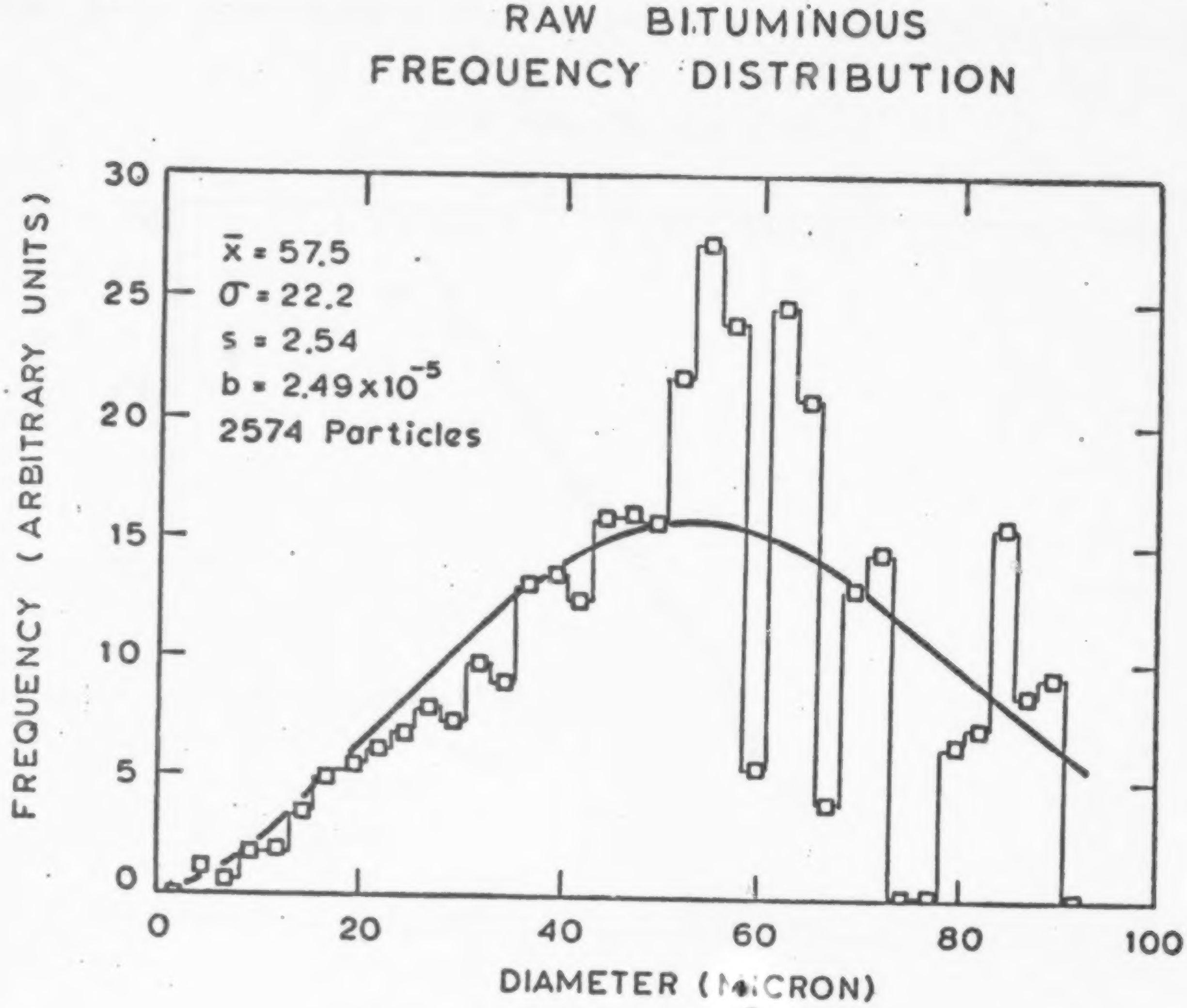


FIGURE IV-8. Bituminous particle size frequency distribution.

IV-2.3 SURFACE AREA

Surface areas, determined using krypton adsorption, are as in the case of lignite significantly below the true surface area, representing only pores with restrictions greater than about 12 A. Calculations of the surface area from krypton adsorption data at 77°K using the Dubinin-Polanyi equation gave 2.1 m^2/g; the BET equation gave 1.25 m^2/g. Gan et al (1972) measured the CO_2 adsorption area for a Pittsburgh seam bituminous coal with 82.4% carbon (dmmf) and found a surface area of 141 m^2/g. This value is consistent with the value of about 150 m^2/g obtained from neon adsorption at 298°K for a coal with 83% C (Dryden, 1963).

IV-2.4 PROXIMATE ANALYSIS

Proximate analyses for the bituminous coal of this study is reported on an as received basis in Table IV-1. The Pittsburgh seam #8 bituminous coal has a low equilibrium moisture content of about 2.2%. This value is taken to be representative of mine samples.

IV-2.5 HEAT OF COMBUSTION

The heat of combustion of the Pittsburgh Seam #8 bituminous coal, determined in the same way as that of lignite, is 14,377 BTU/lb on a moist mineral matter free basis. This value is consistent with other values reported for Pittsburgh seam coals and classifies this coal as a high volatile A bituminous coal.

IV-2.6 ELEMENTAL ANALYSIS

Elemental analysis of the bituminous coal and sulfur form analysis are presented in Table IV-1 on an as received basis, and in Table IV-5 on other commonly used bases. The bituminous coal has 1.04% nitrogen and a high sulfur content of 4.55% on an as received basis. The major portion of the sulfur is pyritic (2.29%) but the organic sulfur is much higher (1.58%) than that of ordinary plant materials. The carbon content is 82.27% on a dry mineral matter free basis.

TABLE IV - 5

BITUMINOUS COAL

CHARACTERIZATION OF PITTSBURGH SEAM #8
BITUMINOUS COAL FROM THE IRELAND MINE
GROUND AND CLASSIFIED TO 38-45μ

COMPONENT	ULTIMATE A.R.	ULTIMATE DRY	ULTIMATE daf	ULTIMATE dmf*	ULTIMATE C-H-O BASIS
H_2O	2.20	-	-	-	-
C	67.90	69.46	77.80	82.27	83.31
H	4.91	5.01	5.62	5.95	6.01
N	1.04	1.06	1.19	1.26	-
Pyritic S	2.29	2.35	-	-	-
SO_4	0.68	0.65	-	-	-
Organic S	1.58	1.52	1.81	1.91	-
Total S	4.55	4.53	-	-	-
ASH	10.52	10.76	-	-	-
O(DIFF.)	8.88	9.19	13.58	8.61	10.87

* Mineral matter found from low temperature ashing by Padia (1976) to be 15.27% (wet basis).

IV-2.7 ASH ANALYSIS

The ash composition of the two coals are compared in Table IV-3. The bituminous coal has a higher ash content than lignite, about 10.5 weight percent versus about 7.8 percent. A very large portion of the bituminous coal's ash is composed of iron compounds, mostly present as pyrites (Padia, 1976). The high pyrites content of the mineral matter accounts for the major portion of the sulfur content of the bituminous coal. Iron, calculated as ferric oxide, accounts for 30% by weight of the ash compared with 38% for silica and 19% for alumina. Calcium, residual sulfur trioxide and potassium are the only other constitutents of consequence in bituminous ash.

IV-2.8 FUNCTIONAL GROUP ANALYSIS

Functional group analysis has not as yet been performed on the bituminous coal sample of this study. A partial functional group analysis has been reported in the literature on a vitrain concentrated sample of a Pittsburgh seam bituminous coal. Heredy and Fugassi (1966) investigated a benzene extract for hydrogen distribution by proton NMR for a vitrain concentrate from the same mine (Ireland) as the bituminous coal used in this study. Their results showed that 16.3% of the hydrogen was substituted on condensed aromatic rings, 14.7% of the hydrogen was attached to either monocyclic aromatic rings or phenolic oxygen; 69% of the hydrogen was attached to aliphatic carbons, 29.6% to α carbons and 39.4% to β carbons. These figures agree only fairly with the figures reported in Table IV-6 and have not been considered in constructing Table IV-6 since the benzene extract accounted for only about 10% of the total coal.

Retcofsky and Friedel (1970) have also investigated functional group distribution of a vitrain rich sample of the coal from a Pittsburgh seam bituminous coal. Their findings are consistent with the results of Tingey and Morrey reported in Table IV-6. Retcofsky and Friedel studied high resolution proton NMR of pyridine and carbon disulfide coal extracts. The pyridine extract contained 21.4% of the coal and had an elemental analysis close to that of the whole coal; the carbon disulfide extract contained only 2.5% of the coal and had significantly higher carbon and hydrogen contents and lower oxygen content than the original coal. Aromatic carbon

TABLE IV-6

FUNCTIONAL GROUP ANALYSIS OF A HIGH VOLATILE BITUMINOUS COAL

From Tingey and Morrey, (1973)
and Dryden, (1963)

	Hydrogen Distribution % of total H	Carbon Distribution % of total C	Oxygen Distribution % of total O
Total daf	5.57	82.4	~9.
Average Ring Size	-	5-8	-
Aromatic	19.6	70.5	-
Monoring	11.2	52.9	-
Condensed Ring	8.4	6.8	-
Peripheral C	-	37.1	-
Interior C	-	33.4	-
Aliphatic	75.7	29.5	-
Methylene Bridges	5.3	6.4	-
α CH_x	36.0	15.4	-
β^+CH_x	37.8	14.1	-
Hydroxyl	4.7	3.8	45.
Carbonyl	-	-	55.
Carboxyl	-	-	0.

accounted for 73% of the carbon in the pyridine extract, 35% of the hydrogen was aromatic, the α aliphatic hydrogen accounted for 26% and β^+ hydrogen accounted for 36% of the total hydrogen. Hydroxyl hydrogen accounted for only 3% of the total hydrogen. The values derived from the carbon disulfide extract were similar although a higher percentage of aliphatic compounds seem to be present in the carbon disulfide extract.

The average ring size of a high volatile bituminous coal with 83% carbon content may be 5-8; the distribution of the carbon may be about 70% aromatic, 30% aliphatic, with only 6% of the carbon in methylene bridges; the distribution of the hydrogen may be 20% aromatic, 75% aliphatic and about 5% in the phenolic OH; the oxygen may be split equally between hydroxyl and carbonyl oxygen with negligible amounts in carboxyl and ether groups.

IV-3.0 PHYSICAL PROPERTIES OF COAL

Estimates of some of the physical properties of coal have been used in this study. These values are not very accurate and have been used only for crude calculations. The values of interest are specific gravity, thermal conductivity, and specific heat. The interpretation of these values for a substance such as coal that is very heterogenous and changes both chemically and physically when mildly heated is questionable. Even when no changes occur in the coal the values are uncertain because the values strongly depend on coal rank, mineral matter content, and moisture content.

Average values of the physical properties needed have been taken from McCabe and Boley (1945), Badzioch *et al* (1964) and Kirov (1965). Specific gravity will increase roughly 0.01 unit for a percent increase in ash content. Thermal conductivity of raw coals below 400°C varies from 5×10^{-4} to 8×10^{-4} cal/g-cm-sec-K. Above about 300-400°C, where carbonization reactions begin, the thermal conductivity rises rapidly until at 900°C (the maximum temperature in Badzioch *et al*'s study) it has a value of about 60×10^{-4} cal/g-cm-sec-K. This high value in all probability represents conductive heat transfer augmented by radiative transfer through pores and convective transfer by volatile products flowing through cracks and pores. The latter two effects are difficult to separate from the former experimentally. The thermal conductivity of the particle is needed for purposes of calculating the rate of temperature rise in the particle. Since the resistance to heat transfer by conduction within the particle is negligible relative to the external resistance, uncertainty in the value of the thermal conductivity is of little significance.

Measurements of specific heat will also be effected by the heterogeneous nature of coal and by the physical and chemical changes coal goes through as it is heated. The specific heat of raw coal increases with increasing volatile matter and increasing moisture content and decreases with increasing ash content. The specific heat of raw coals with less than 10% volatile matter (d.a.f.) will be between 0.2 and 0.25 cal/g-K, while coals with volatile matter (d.a.f.) between 10 and 50% will have specific heats between 0.25 and 0.35 cal/g-K. Coals with volatile matter in the range of 40% (d.a.f.) will have specific heats around 0.3cal/g-K.

Char residuals (based on weight of raw coal) could have a maximum specific heat of 0.42 cal/g-K at 320°C for a char from a coal with 50% d.a.f. volatile matter. The specific heat of chars produced from coals with volatile matter (d.a.f.) greater than 30% have a specific heat maximum in the region of rapid devolatilization. The specific heat then decreases towards an asymptotic value at temperatures above 1100°C. The position of the specific heat maximum is displaced towards higher temperatures as the volatile matter of the coal decreases. Chars produced from coals with d.a.f. volatile matter in the range of 30-40% would be expected to have a specific heat value of about 0.33 cal/g-K based on the weight of the raw coal.

IV-4.0 CHARACTERIZATION OF OTHER COALS AND CHARS

Most experiments were run using the carefully characterized lignite and bituminous coals described in Sections IV-1.0 and IV-2.0. Several additional experiments were performed using a Montana sub-bituminous coal. Char oxidation experiments utilizing chars prepared from the Montana Lignite were also performed. Proximate and ultimate analyses of these additional samples are shown in Table IV-7.

TABLE IV-7. CHARACTERIZATION OF COALS AND CHARS

		Proximate Analysis A.R. Wt%			Ultimate Analysis A.R. Wt%				
Type	Specification	VM	H_2O	Ash	C	H	N	S	O (by Diff.)
Montana Lignite-A	Savage	36.20	13.60	7.80	54.40	4.96	0.88	0.84	17.42
Montana Sub-bituminous**	Powder River Region	35.16	21.23	9.34	53.26	3.35	0.87	0.78	11.17
1250 K Lignite Char		NM*	4.20	12.08	66.94	2.09	1.02	0.56	13.11
1750 K Lignite Char		NM	2.02	18.03	76.42	0.69	0.55	1.06	1.23
1750 K Lignite Char***		NM	2.10	19.00	76.11	0.36	0.58	1.11	0.74

*NM = Not Measured

**Supplied by Aerotherm Division of Acurex Corporation

***Used in time resolved measurements.

SECTION V

COAL RESULTS

This section reports the results obtained on evolution and oxidation of nitrogen contained in coal using the equipment and procedures described in Section III. The results described include nitrogen loss from coal held in crucibles, nitrogen loss from coal rapidly heated in the dispersed phase, and conversion of coal and char nitrogen to nitric oxide when burned in a small coal flame.

V-1.0 THE COAL FLAME- MOTIVATION FOR THE EXPERIMENTS

Coal supplies slightly over half of the fossil fuel burned to generate electric power. Its use can be expected to increase as the other fossil fuels become less abundant and more costly. Most of the coal burned for power generation is burned in pulverized coal flames in large units (hundreds of megawatts electrical capacity). Combustion of coal yields higher emissions of sulfur dioxide, particulate matter, and nitrogen oxides than other fuels. The data reported in this section were taken in an effort to understand some of the complex aspects of the oxidation and reduction of the nitrogen contained in the coal with the ultimate goal of investigating strategies for control of the fuel nitrogen contribution to total nitrogen oxide emissions.

A schematic of a pulverized coal flame is shown in Figure V-1. Coal is ground to less than 200 micron particles (most particles

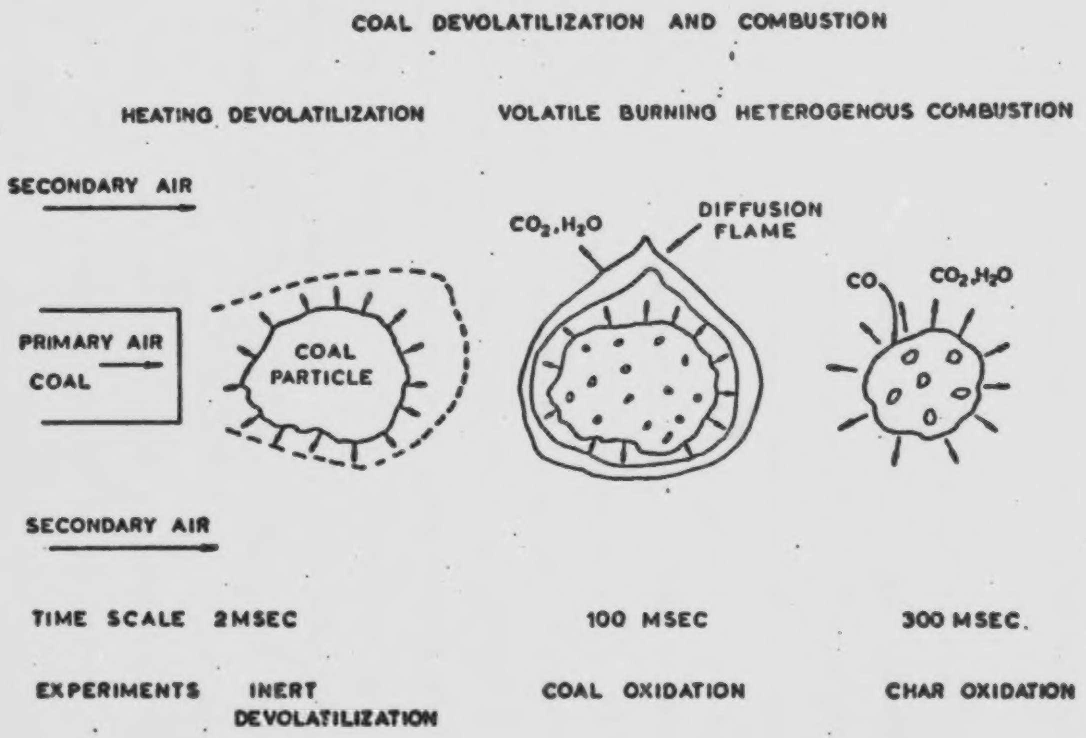

COAL DEVOLATILIZATION AND COMBUSTION
HEATING DEVOLATILIZATION
VOLATILE BURNING
HETEROGENOUS COMBUSTION
SECONDARY AIR
CO_2, H_2O
DIFFUSION FLAME
CO
CO_2, H_2O
PRIMARY AIR
COAL
COAL PARTICLE
SECONDARY AIR
TIME SCALE
2MSEC
100 MSEC
300 MSEC.
EXPERIMENTS
INERT DEVOLATILIZATION
COAL OXIDATION
CHAR OXIDATION

FIGURE V-1. Schematic of a single coal particle burning in a pulverized coal flame.

are less than 100 microns), and fed through the primary injection nozzle. A fraction of the total air (usually 15-20% of the stoichiometric air requirements) is used to carry the coal into the flame region. A large 500 mw utility boiler typically feeds about 200 tons/hr coal and 3300 tons/hr air. If four burners are used, each burner will be fed 50 tons/hr coal and about 50 tons/hr air through the primary nozzle. The remaining air is preheated and fed through swirl vanes surrounding the primary nozzle.

The coal particles exit the nozzle in a slightly fuel rich atmosphere. The reducing nature of this atmosphere is increased further by recirculation of partially combusted gases from the flame region. The coal particles are heated, possibly as high as 2200°K, by the hot recirculating gases in about one millisecond. The coal particle rapidly loses volatile matter over the next tens of milliseconds. This volatile matter, depending on the velocity and uniformity of ejection, can exclude oxygen from the particle surface and burn as a diffusion flame surrounding the particle. The volatile matter may not be able to form an effective oxygen shield in all cases, and the particle will simultaneously undergo gas phase volatile matter burning and heterogeneous solid phase combustion. Burning of the volatile matter is usually complete in about 100 milliseconds.

Volatile burning will leave a char residue, even if the solid has been burning simultaneously with the volatile matter. The char will be heterogeneously oxidized in about 300 milliseconds.

Experiments that might be used to isolate the different regions of coal combustion are listed at the bottom of Figure V-1. Volatile matter removal can be investigated by devolatilizing coal under conditions of reduced oxygen concentration which supress ignition of the particle. Devolatilization of coal particles under inert atmospheres will be reported in this section. Coal oxidation under the condition when the coal particle is surrounded by a diffusion flame of the volatile matter can be investigated by burning the coal particle in a dilute phase so that particles have little interaction with each other. Only overall oxidation experiments where the coal particles burn as small diffusion flames are reported in this section. Char oxidation kinetics can be investigated by manufacturing the char in an atmosphere where the coal particles will not ignite and then reinjecting the coal particles into an oxidizing atmosphere where the particles burn heterogeneously as individual particles. Some results from char oxidation are reported in this section. The gas phase reactions of the products produced from coal devolatilization and partial combustion, descriptions of which are needed to complete the picture of the oxidation of the nitrogen content in coal, are best studied in simplified systems such as flat flame burners, and do not constitute part of the present study.

V-2.0 DEVOLATILIZATION RESULTS

Coal pyrolysis studies include asymptotic elemental and total weight loss from crucible held samples as well as time-resolved weight loss experiments conducted in the flow reactors for residence times up to one second. Limited analyses of gas-phase pyrolysis products are also presented in an attempt to close the carbon and nitrogen material balances.

V-2.1 DEVOLATILIZATION RESULTS FROM CRUCIBLE EXPERIMENTS

The purpose of the crucible experiments is to investigate the effect of temperature on the behavior of coal devolatilization in inert atmospheres at long residence times. The nature of the experiments precluded the attainment of the rapid heating conditions typically found in pulverized coal flames. Heating rates were typically on the order of several degrees Kelvin per second. The data reported here are for times at which the coal weights had reached their asymptotic values.

V-2.1.1 PITTSBURGH SEAM #8 hvA-BITUMINOUS COAL

Figure V-2 shows the retention of various elements in the coal and ultimate weight loss for crucible held coal as the temperature increases from 600 to 2200°K. The chars were analyzed after times considered to represent asymptotic weight loss and are represented on a dry basis. The weight loss for temperatures above about 1200°K is asymptotic at about 40%, below 1200°K the weight loss drops. The weight loss observed after 12 hours at 600°K is only about 10%. Carbon loss levels off at 1200°K, when the weight loss is about 30%. Hydrogen is initially removed more slowly than oxygen but after both oxygen and hydrogen contents of

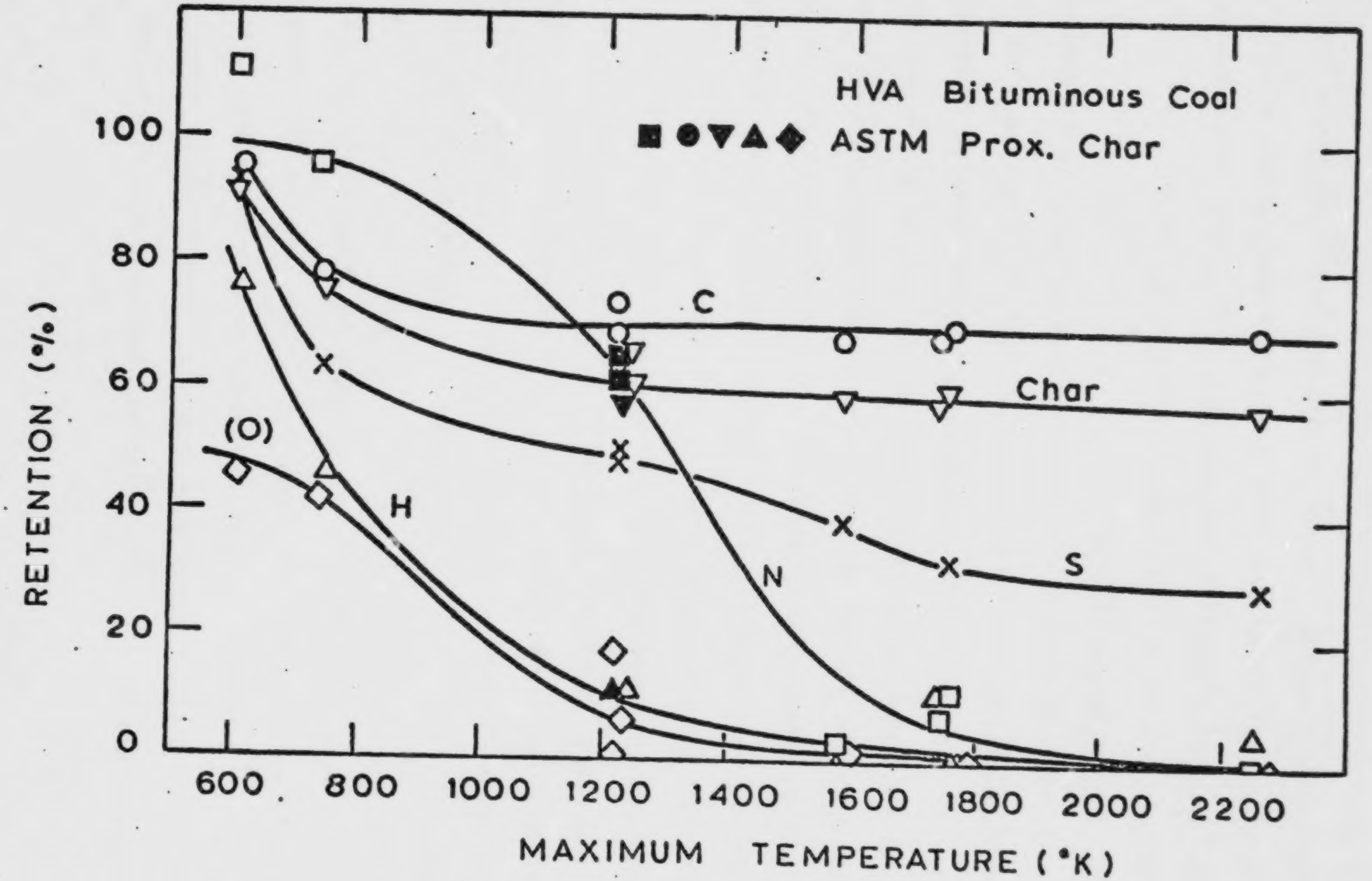


FIGURE V-2. Crucible devolatilization of Pittsburgh Seam #8 hv A-bituminous coal.

the char have dropped to about 40% of their original values, the rate of fractional loss of hydrogen and oxygen become approximately equal. Oxygen, hydrogen, and nitrogen are completely removed from the char at high temperatures, under the conditions of asymptotic weight loss. Nitrogen is much more stable in the char than either hydrogen or oxygen.

V-2.1.2 MONTANA LIGNITE-A

Element loss from the lignite samples held in crucibles is shown in Figure V-3. The retention trends of the various elements are very similar to the trends observed for similar experiments using the bituminous coal. The proximate analysis volatile matter, dark symbols, agrees well with the ultimate weight loss obtained by slowly heating coal samples. Carbon loss and total weight loss increase only slightly above the proximate analysis temperature of 1223°K. The asymptotic carbon loss was about 20% although the carbon loss appeared to increase slightly as the devolatilization temperature increased above 1700°K. The char showed no additional weight loss above about 1600°K. The asymptotic weight loss was 44% which is only slightly greater than the proximate volatile matter of 41%. Little weight loss of carbon occurs at low temperatures.

Oxygen, hydrogen, and nitrogen are completely removed at high temperatures. Hydrogen and oxygen loss as the percent of the element originally present are very nearly the same. Initially there is approximately five times as much hydrogen present as oxygen on a mole basis. Hydrogen and oxygen contents are reduced

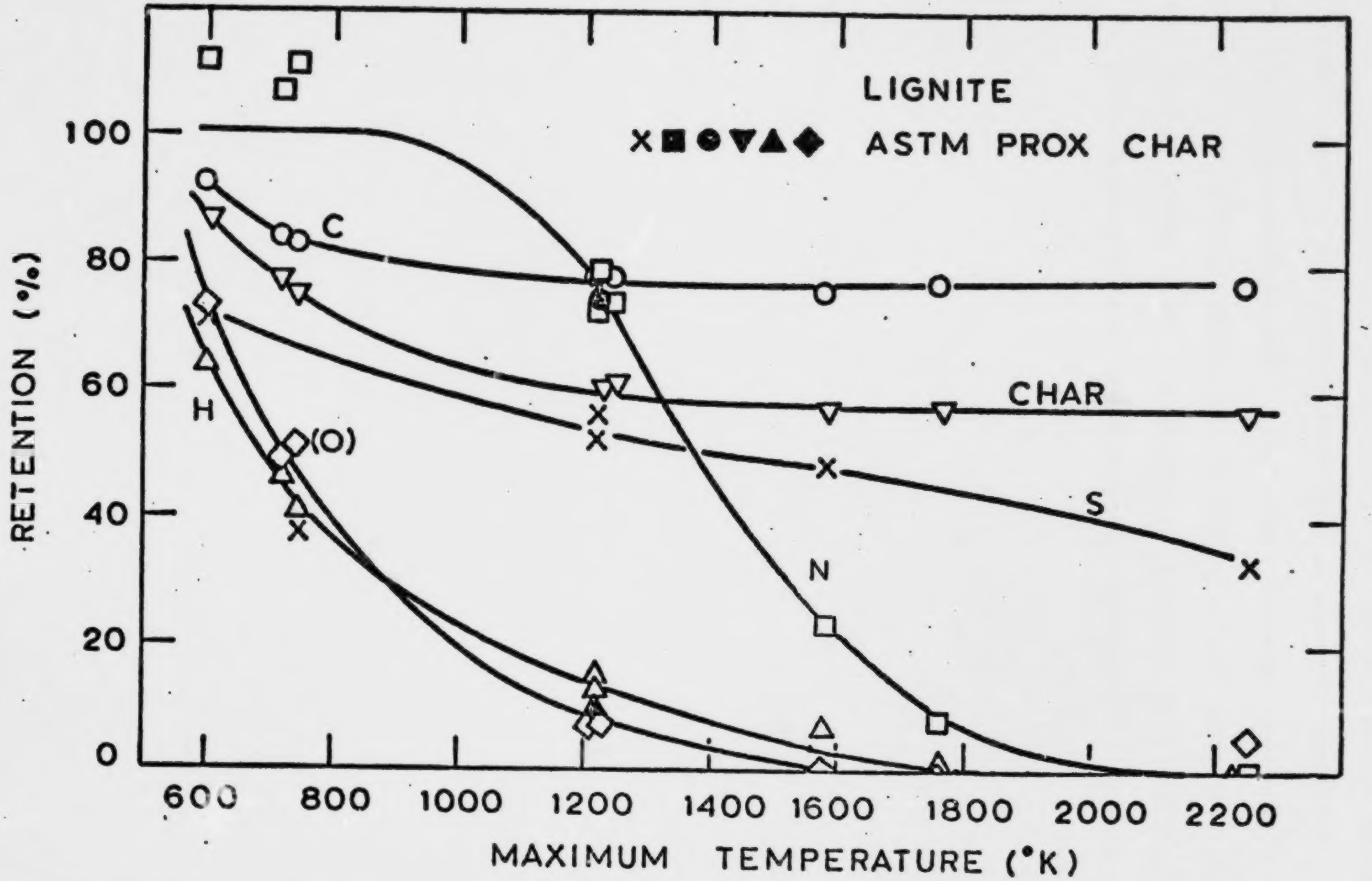


FIGURE V-3. Crucible devolatilization of Montana lignite-A.

to low values at temperatures in the range of 1600°K and are both reduced to zero above 1800°K.

Nitrogen is, again, the most refractory of the elements that are completely removed from coal. The lignite coal used in this study has approximately 28% of the original nitrogen removed under proximate analysis conditions. This value agrees well with the amount of nitrogen removed under the crucible tests of this study.

V-2.2 DEVOLATILIZATION OF DISPERSED COAL PARTICLES

Experiments were conducted on devolatilization of coal falling freely through an inert gas surrounded by hot walls. The purpose of this set of experiments was to obtain devolatilization data for coal that is rapidly heated ($\sim 10^4$°K/sec) in a dispersed phase for relatively long residence times, on the order of one second. A slight modification of this experiment was used to gather data on rapidly heated coal devolatilization at longer residence times by dropping the coal into a crucible where further devolatilization of the char occurs on a sample held at the maximum temperature of the experiment.

V-2.2.1 PITTSBURGH SEAM #8 BITUMINOUS COAL

Data gathered on element loss from the bituminous coal under a variety of experimental conditions, including free fall conditions, is shown in Figure V-4. The free fall data has a residence time of approximately one second and the free fall into a crucible data has residence times varying from 3×10^4 to 6×10^5 seconds. The laminar flow experiments gave devolatilization residence time from several milliseconds to a maximum of about 300 milliseconds. The long residence time data is replotted from the crucible experiments discussed in Section V-2.1.1.

The retention of the various elements are plotted in Figure V-4 versus time in milliseconds with furnace temperature as a parameter. A log time scale is used so that the data can be represented on one plot. The retention of each element (weight percent of the original element retained after devolatilization)

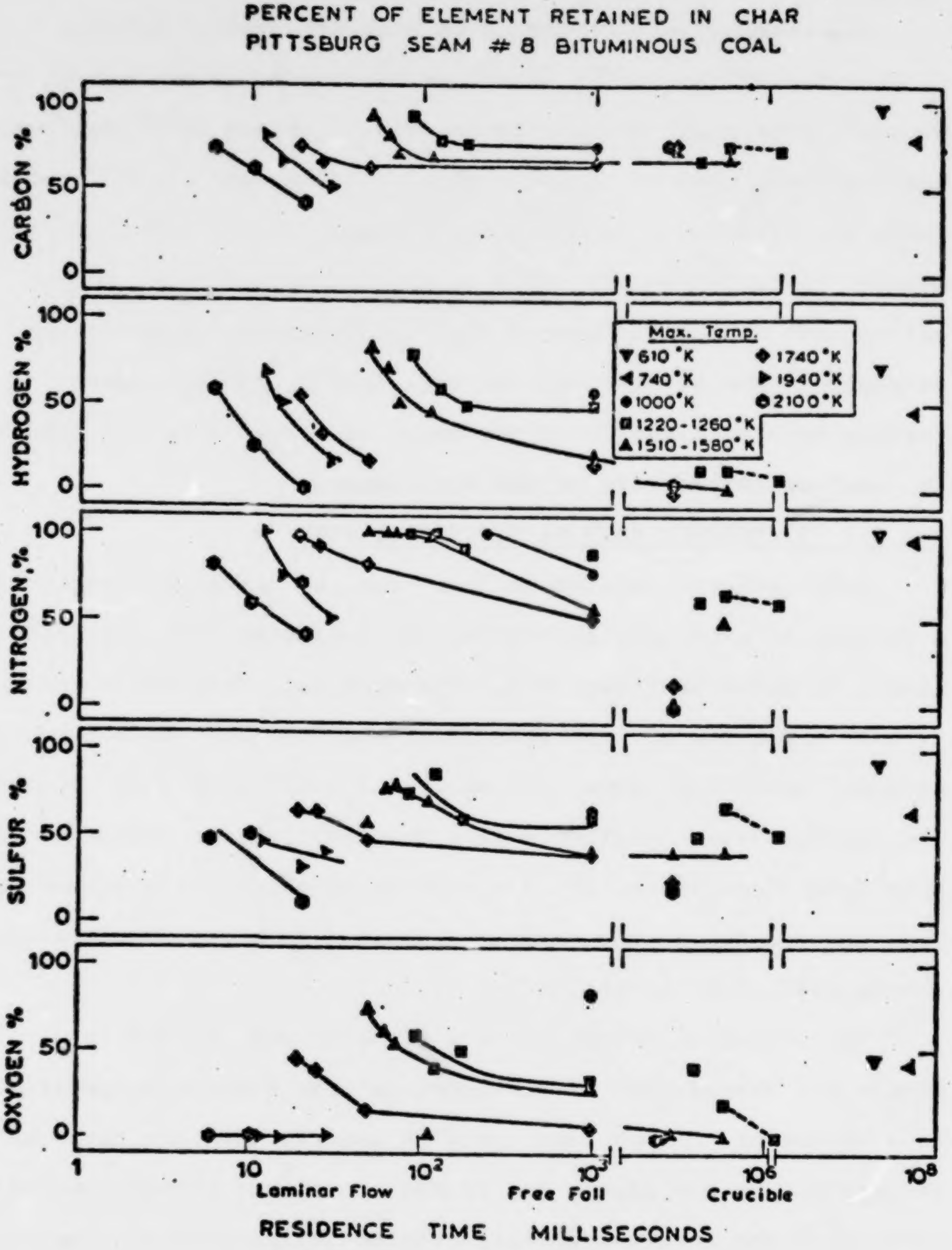


FIGURE V-4. Element loss with devolatilization of a Pittsburgh Seam #8 hvA-bituminous coal.

is plotted with a common time axis to facilitate comparisons of the stability of the different elements in the coal matrix. The solid lines extended past one second represent retention of the element for coal that has been dropped through the furnace, caught in a crucible, and held at furnace temperature for the time indicated. The dotted lines connecting two points represent the change in retention with additional devolatilization when the char produced at the shorter residence time is reinjected into the furnace and held at the same temperature for additional time.

An asymptotic carbon retention of 75% was approached at 300 milliseconds for 1260°K, of 65% at 100 milliseconds for 1510°K, and of 60% at 50 milliseconds for 1740°K. Although the total weight loss appeared to attain an asymptotic value of 52% dry at 1940°K and 32 milliseconds and 57% dry at 2100°K and 21 milliseconds, the carbon loss does not appear to be complete. This implies that further slow carbon loss might be obtained at longer residence times at these high temperatures. The carbon retention was about 50% at 32 milliseconds and 1940°K and about 40% at 21 milliseconds and 2100°K. Kobayashi (1976) presents a more complete discussion of the same data.

Hydrogen is relatively easy to remove from coal during pyrolysis. Below 1260°K, hydrogen loss is relatively rapid until about 50% of the hydrogen has been removed; the remaining hydrogen is removed much more slowly. However, hydrogen can be almost completely removed at 1260°K for residence times on the order of ten minutes. At high temperatures the complete removal of hydrogen is rapid, 21 milliseconds at 2100°K. Large quantities of hydrogen are still retained in the char after pyrolysis at 740°K for 22 hours. Slow evolution of hydrogen probably continues for even longer periods at 740°K, unless further evolution of hydrogen is constrained by thermodynamics.

Nitrogen is the most difficult element to ultimately remove from the coal matrix after carbon. At low temperatures, around 700°K. nitrogen loss is very small; at 1260°K nitrogen loss is also small but can be seen to continue at a slow rate by the two square points joined by dotted lines. Nitrogen removal is complete at temperatures above 1500°K at long, but reasonable residence times, as indicated by the data around five minutes residence times. Nitrogen removal by pyrolysis and oxidation is the major concern of this study and will be discussed in more detail from an expanded plot of nitrogen removal.

Sulfur is not as difficult to remove from coal as carbon and nitrogen, but is more difficult to remove than hydrogen and oxygen. The data indicates that at temperatures below about 1900°K sulfur removal is slow once 50% of the sulfur has been removed. The amount of sulfur easily removed from coal is apparently temperature dependent. The asymptotic retention of sulfur in the char at 1260°K is about 70% but at 1510 and 1740°K is about 40%. Sulfur was almost completely removed at 2100°K and 21 milliseconds.

Oxygen appears to be slightly easier to remove than hydrogen at higher temperatures but somewhat more difficult to remove at lower temperatures. All the oxygen can be removed at 1260°K and ten minutes residence time or at times less than 7 milliseconds at 1940°K. Slow evolution of oxygen at 1260°K is evident from the decrease in oxygen concentration between the two points connected by a dotted line.

V-2.2.2 MONTANA LIGNITE

Data on the element retention of devolatilized lignite (shown in Figure V-5) used in this study versus residence time at different furnace temperatures is similar to the results for the bituminous coal just presented. The release of hydrogen appears to be more rapid under certain conditions for lignite than bituminous coal; all the other elements showed a similar behavior for bituminous coal and lignite. The curves for element retention are, in general, similar in shape and magnitude to the retention curves developed for bituminous coal.

Carbon loss appears to become asymptotic for all temperatures at about 100 milliseconds. The asymptotic carbon retentions are: 75-80% at 1260°K, 65% at 1510°K, 55-60% at 1740°K, ∿50% at 1940, and ∿40% at 2100°K. Little additional carbon appears to be removed under conditions of low temperature and long residence times.

Hydrogen loss is complete at either moderate temperatures and long residence times or high temperatures and short residence times. For example, hydrogen was completely removed from char devolatilized at 1750°K for five minutes or at 2100°K for 30 milliseconds. Hydrogen is more easily removed from lignite than from bituminous coal at temperatures below 1510°K; above this temperature the rate of hydrogen removal from the two coals appears to be approximately equal.

Nitrogen, as for bituminous coal, is the element most resistant to ultimate devolatilization after carbon. The rates of nitrogen removal from bituminous coal are slightly faster than from lignite at all temperatures. The difference is, however, not great. The

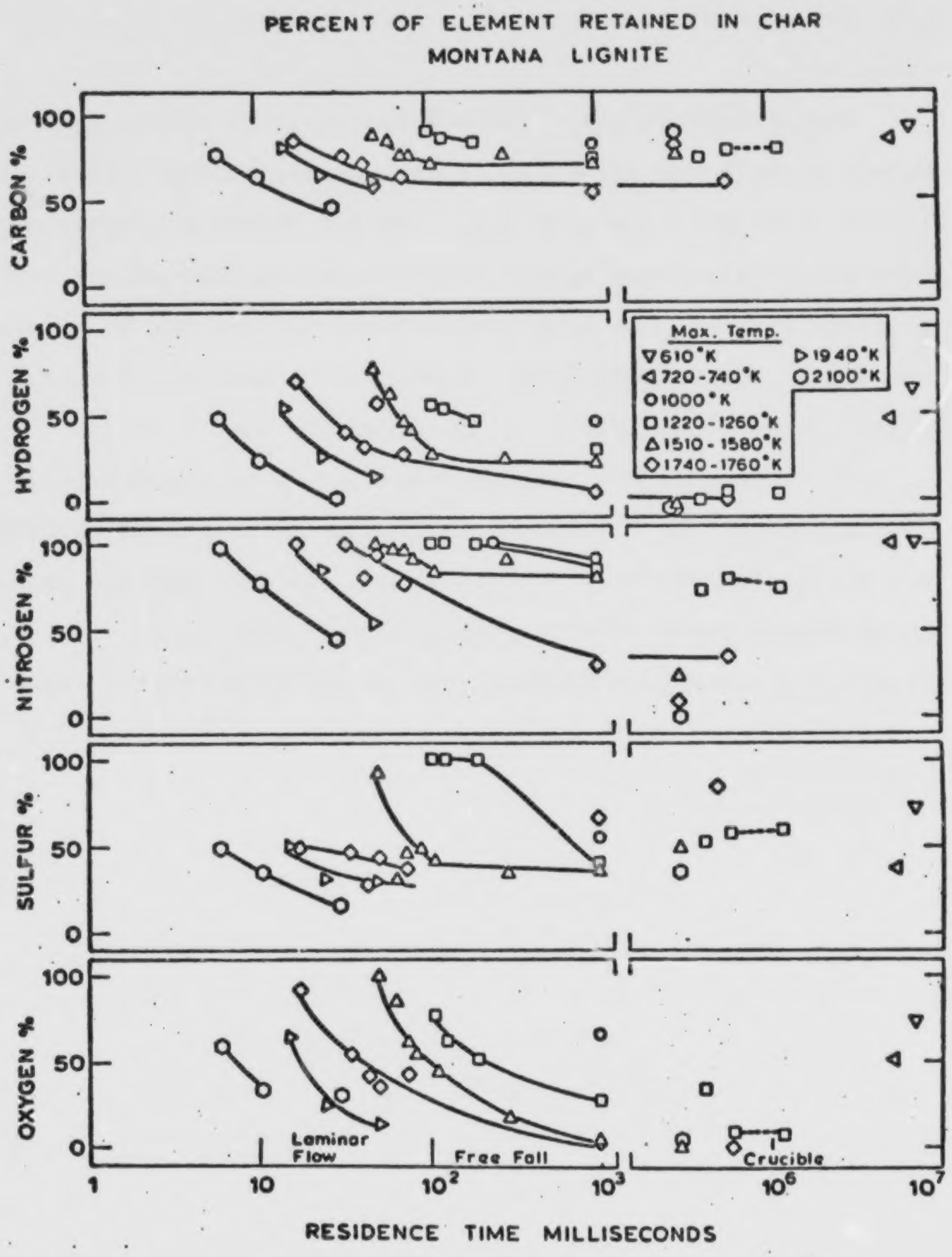


FIGURE V-5. Element loss with devolatilization of a Montana lignite-A.

nitrogen removal from both coals is discussed in more detail later.

The percent removal from the two coals of sulfur show similar behavior, with the exception of the greater sulfur removal at 1260°K from the bituminous coal. As for bituminous coal, sulfur removal is relatively slow. Indications are that sulfur can be completely removed at high temperatures but can not be effectively removed at low temperatures. Asymptotic retention of sulfur at temperatures below 1510°K is approximately 50%.

Percentage oxygen removal from lignite is approximately equal to the removal for bituminous coal at temperatures below 1510°K, but oxygen removal from bituminous coal is considerably faster at temperatures above 1940°K. Oxygen can be completely removed within reasonable times from lignite char at all temperatures above 1260°K.

V-2.2.3 NITROGEN PYROLYSIS FROM LIGNITE AND BITUMINOUS COAL

The nitrogen retention data from Figures V-4 and 5 for the fast flow and free fall experiments is replotted in Figure V-6 with expanded scales. The retention data at 1260°K for the bituminous coal shows some scatter.

There are two features of the retention curves for lignite that also should be noted. One datum point has higher retention than a smooth curve through the rest of the data would indicate. This point was obtained in an attempt to increase the residence time of the fast flow furnace past the residence times that the furnace yielded when operated in the normal mode. The plasma gun could not be used to heat the large quantity of gas used to carry the particle at the low flow rate required; it is, therefore, likely that this point had a significantly lower temperature than the rest of the data at 1510°K. Two data points taken at a temperature of 1740°K and short residence times show approximately the same small nitrogen loss. The nitrogen content of the original coal has been checked many times but, the nitrogen content determined by the Dumas method gave consistantly lower results than the nitrogen content determined by the Kjeldahl method. This can only be caused by incomplete reduction of nitrogen oxides generated during the burning of coal in the Dumas method. The Dumas method gave nitrogen results about 20% lower than the Kjeldahl method for lignite, digestion of the nitrogen compounds from butuminous coal is known to be more difficult (Jodidi (1910) and Shacklock and Drakeley (1927)) so the nitrogen content of the bituminous coal was measured using

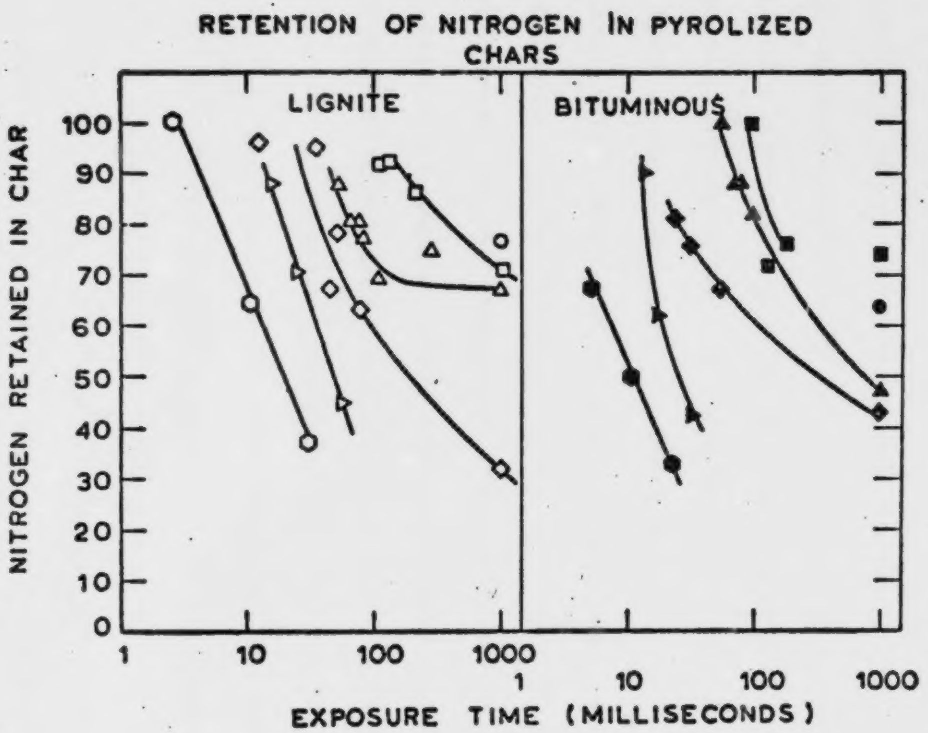


FIGURE V-6. Retention of nitrogen in devolatilized lignite and bituminous coal chars.

a 24 hour Kjeldahl digestion. Use of the nitrogen contents determined by the Dumas method gave inconsistent results for nitrogen in the early stages of devolatilization, therefore the higher Kjeldahl results for nitrogen content of the original coal have been used. Even when the Kjeldahl results are accepted there is a residual uncertainty in the nitrogen measurements. This uncertainty could indicate that the two points showing nitrogen retention of approximately 97% actually represent conditions where no nitrogen evolution occurs; this explanation agrees with the hypothesis on nitrogen devolatilization to be presented in the discussion section.

Figure V-6 shows more clearly that nitrogen is a very refractory element in coal. At the most extreme conditions of the experiments presented here, no more than 70% of the nitrogen has been removed after one second. Additionally nearly all the nitrogen is retained in the char for an induction period that depends on temperature. Bituminous coal has an induction period of about 100 milliseconds at 1260°K, 60 at 1510°K, ∿20 at 1740°K, 12 at 1940°K, and near zero at 2100°K. The induction times for lignite are: 100 milliseconds at 1260°K, 30 at 1510°K, 20 at 1740°K, 10 at 1940°K, and 2 at 2100°K. The induction times for lignite and bituminous coal appear to be consistent considering that some extrapolations were necessary.

The nitrogen retention for lignite at 1510°K levels off at 67% and about 100 milliseconds. The shape of the curve appears different when compared with the rest of the data. However, the asymptotic value at one second is very well established so the shape of the curve must be nearly correct.

V-2.3 ANALYSIS OF VOLATILE PRODUCTS OF COAL PYROLYSIS

A set of experiments was conducted in which the gas-phase products of coal pyrolysis were partially analyzed in an attempt to determine the fate of the carbon and nitrogen evolved from the coal. The lignite coal in a 38-44 micron size cut was fed into the free-fall reactor under an inert atmosphere of helium, and with a residence time in the hot zone of about one second. Off-gases from the furnaces were collected in a gas sampling bag for gas chromatographic analysis, or bubbled through scrubbers for electrochemical analysis. The reader is referred to Section III-4 for a review of the analytical procedures. Results pertinent to the carbon and nitrogen material balances are shown in Figures V-7 and V-8 respectfully and summarized in Tables V-1 and V-2.

The carbon material balance cannot, of course, be closed by the limited analyses performed, insofar as hydrocarbons other than methane are not accounted for and tars, known to form under these conditions are, likewise, not detected. However, in view of Suuberg's recent results (1977), tar and heavier hydrocarbon contributions can be roughly estimated, as shown in Table V-1, yielding a generally satisfactory closure of the carbon material balance. HCN contributes negligibly.

Closure of the nitrogen balance is somewhat less certain, however, because of large instrumental uncertainties in the analysis for N_2 as well as the possiblity of evolution of nitrogen bearing species other than those indicated (N_2, HCN, NH_3). No NO was detected (detection limit: -2.5 ppm) under the conditions of the

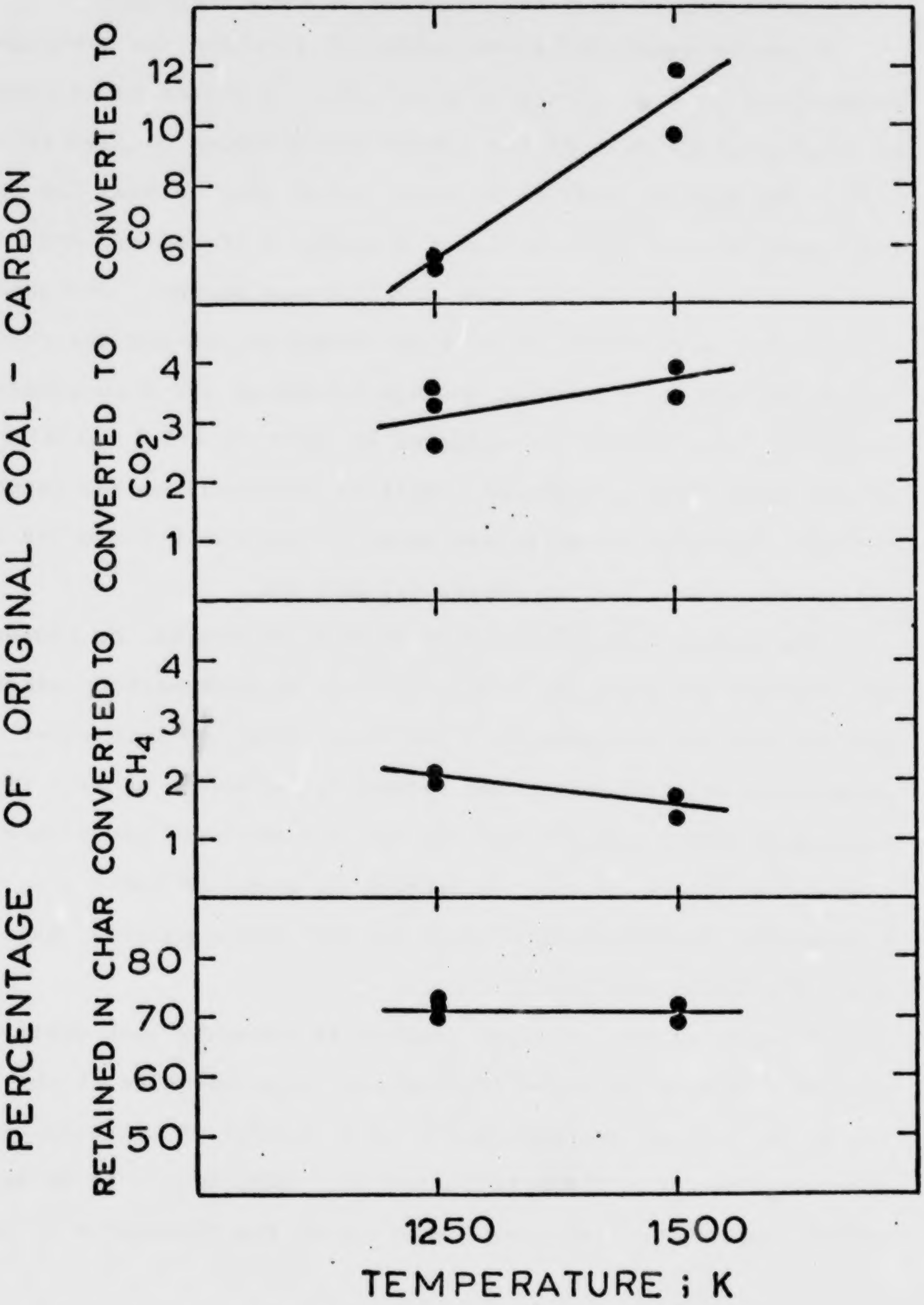

PERCENTAGE OF ORIGINAL COAL - CARBON
CONVERTED TO CO
12
10
8
6
CONVERTED TO CO2
4
3
2
1
CONVERTED TO CH4
4
3
2
1
RETAINED IN CHAR
80
70
60
50
1250
1500
TEMPERATURE ; K

FIGURE V-7.

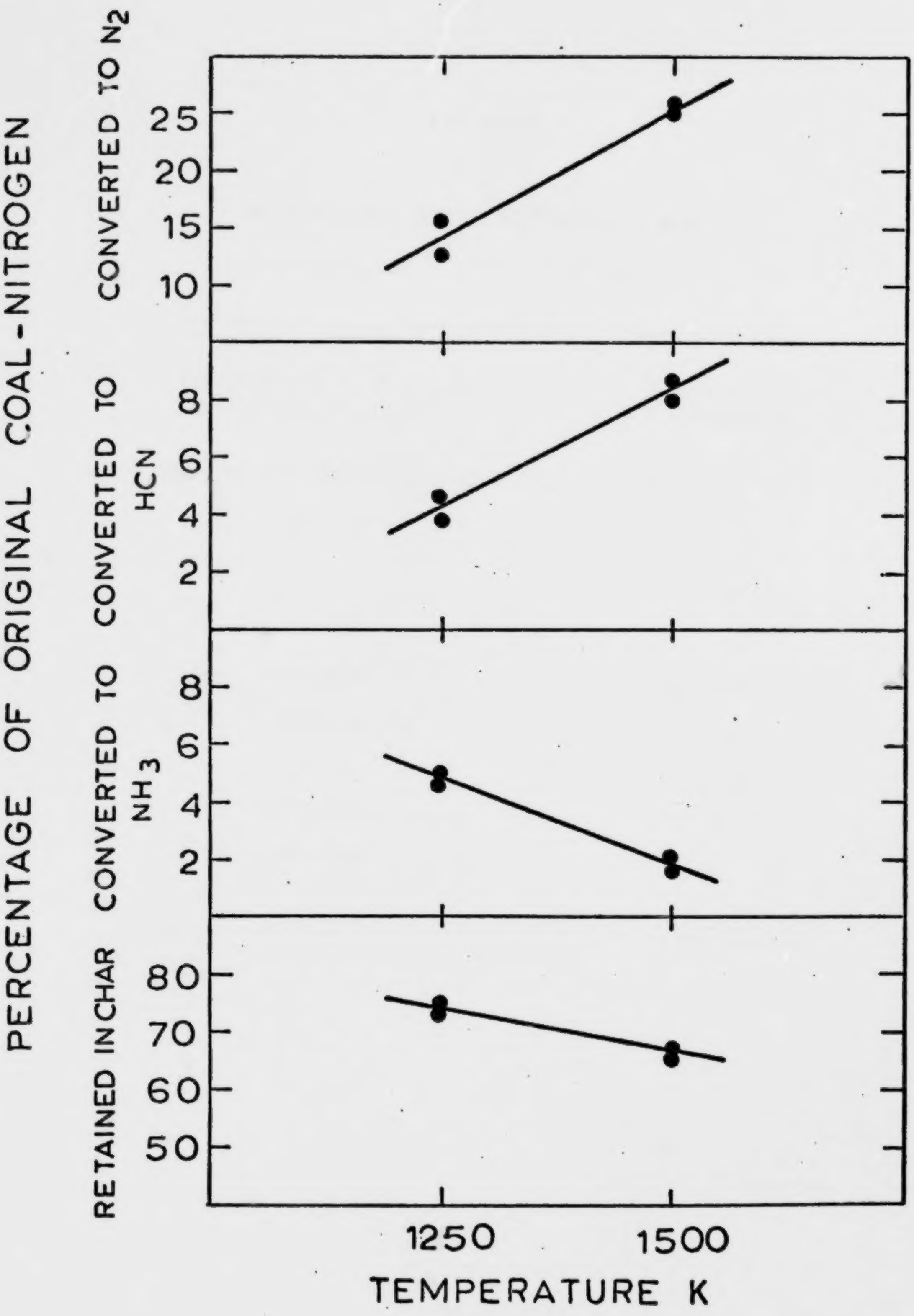

PERCENTAGE OF ORIGINAL COAL-NITROGEN
CONVERTED TO N_2
10
15
20
25
CONVERTED TO HCN
2
4
6
8
CONVERTED TO NH_3
2
4
6
8
RETAINED IN CHAR
50
60
70
80
1250
1500
TEMPERATURE K

FIGURE V-8.

TABLE V-1

CARBON DISTRIBUTION DURING COMBUSTION OF LIGNITE AT T=1750 K and $\phi=3\sim4$

Combustion Products	Weight % of the Original Carbon in Lignite
CO	72 ~ 75
CO_2	11 ~ 16
CH_4	1 ~ 2
Other CH	Not Measured
TAR	Not Measured
Char	4 ~ 5
Total	88 ~ 98

TABLE V-2

NITROGEN DISTRIBUTION DURING COMBUSTION OF LIGNITE AT T=1750 K AND $\phi=3\sim4$

Combustion Products	Weight % of the Coal-Nitrogen in Lignite
N_2	71 ~ 75
HCN	6 ~ 8
NH_3	Trace
NO_x	1 ~ 3
Char	3 ~ 5
Total	81 ~ 91

experiment. Furthermore, reported HCN levels may not strictly represent primary yields of HCN as additional experiments provide indication of thermal decomposition of HCN at the highest temperature conditions in the furnace. The results in this section show the consequence of both primary pyrolysis of the coal and secondary pyrolysis of the volatile products. They are reported to provide a measure of confidence in the data on the char through an ability to close a material balance.

V-3.0 OXIDATION RESULTS

In order to investigate the regime of volatile burning and heterogeneous combustion depicted in Figure V-1, the burning and conversion of coal nitrogen to nitric oxide for both raw and devolatilized coal were investigated. The premise of conducting oxidation experiments on both char and coal was that if volatile burning and char burning could be treated as nearly independent, then the contribution of the volatiles to total nitric oxide could be obtained by subtracting the contribution of char oxidation from the total nitric oxide emission obtained form oxidation of the raw coal.

V-3.1 OXIDATION OF LIGNITE AND BITUMINOUS COAL-FIXED RESIDENCE TIME

Lignite and bituminous coal were burned in 21% oxygen in helium mixtures at varying percentages of the stoichiometric oxygen requirement at three different temperatures according to the procedure outlined in Section III-2. The unburned char was recovered and residual combustibles and nitrogen were determined. Nitrogen oxide production was determined by measuring the concentration of the gas effluent from the furnace.

The results obtained from oxidizing raw coals at various fuel equivalence ratios in a 1500°K furnace are shown in Figure V-9. Little difference was apparent in nitrogen converted to nitric oxide and nitrogen retained in the char for the two coals and the limited number of particle sizes studied. There is some indication that the burnout of bituminous coal may be more difficult than the burnout of lignite.

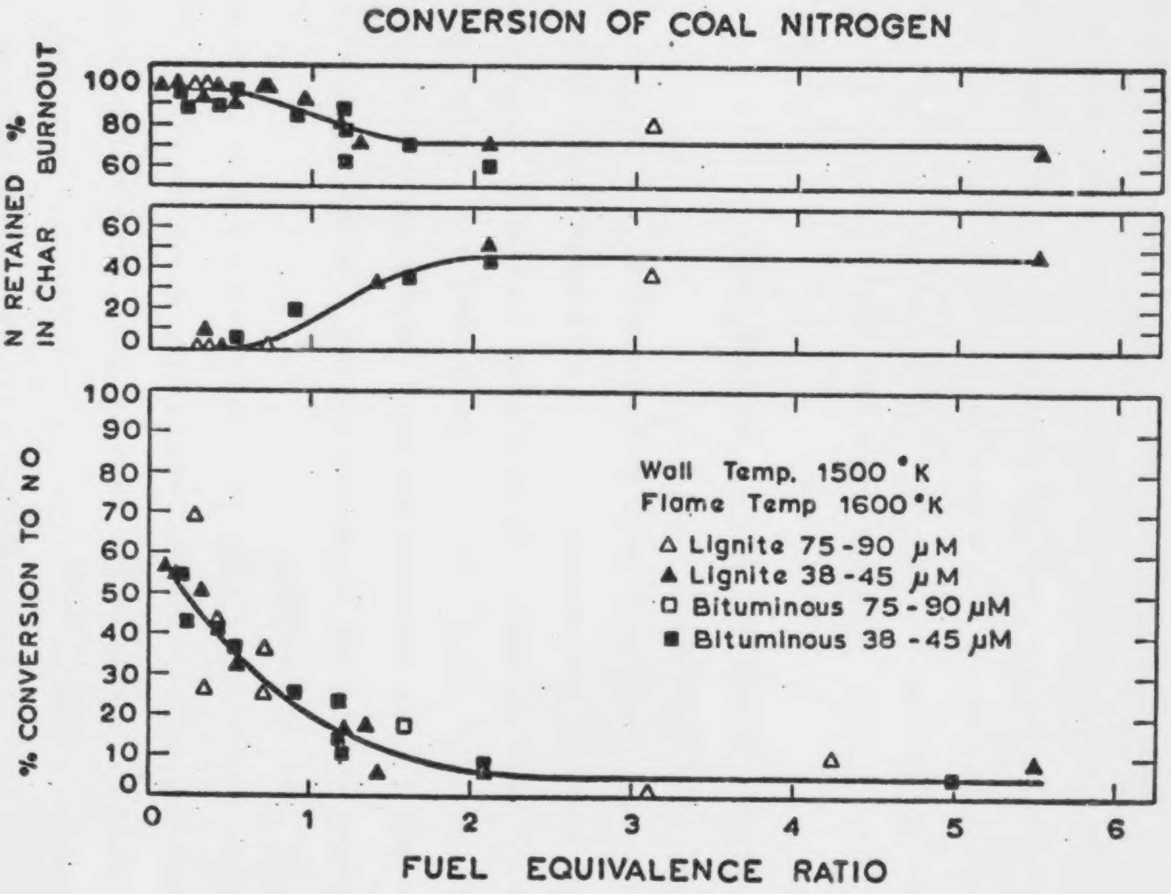


FIGURE V-9. Conversion of coal nitrogen as a function of fuel equivalence ratio in a 1500°K furnace.

As expected, the char burnout is near 100% at lean conditions but residual char remains as the fuel equivalence ratio approaches stoichiometric and burnout continues to decrease until an asymptotic value of about 70% at a fuel equivalence ratio of 1.5 is obtained. Nitrogen retained in the char follows a curve complimentary to the burnout curve. When char burnout is complete there is obviously no nitrogen retained in the char; however, when char oxidation is incomplete nitrogen is retained in the residual char. Nitrogen retained in the char reaches an asymptotic value of 45% at fuel equivalence ratios above 1.75.

The conversion of fuel nitrogen to nitrogen oxides approaches 60% at very lean fuel equivalence ratios but decreases as fuel equivalence ratio increases. At a fuel equivalent ratio of 0.7 the conversion of fuel nitrogen to nitrogen oxides is about 30%, at 1.2 about 15% and above 2 the conversion is asymptotic at about 5%.

Similar conversion of lignite in a 1750°K furnace is shown in Figure V-10. Several differences are apparent between the oxidation of coals at 1500°K and at 1750°K:

1) Burnout at the higher temperature is complete even at a fuel equivalence ratio of 1.5, and even at very rich conditions the burnout is still 95%. This may be indicative of an oxidative pyrolysis mechanism and

2) The conversion efficiency of fuel nitrogen to nitrogen oxides is marginally lower: about 5 absolute percent.

The conversion of fuel nitrogen to nitrogen oxides was about 60% at very lean fuel equivalence ratios, 22% at 0.7, 10% at 1.2, and reaches an asymptotic conversion efficiency of about 1% for fuel equivalence ratios above 2.

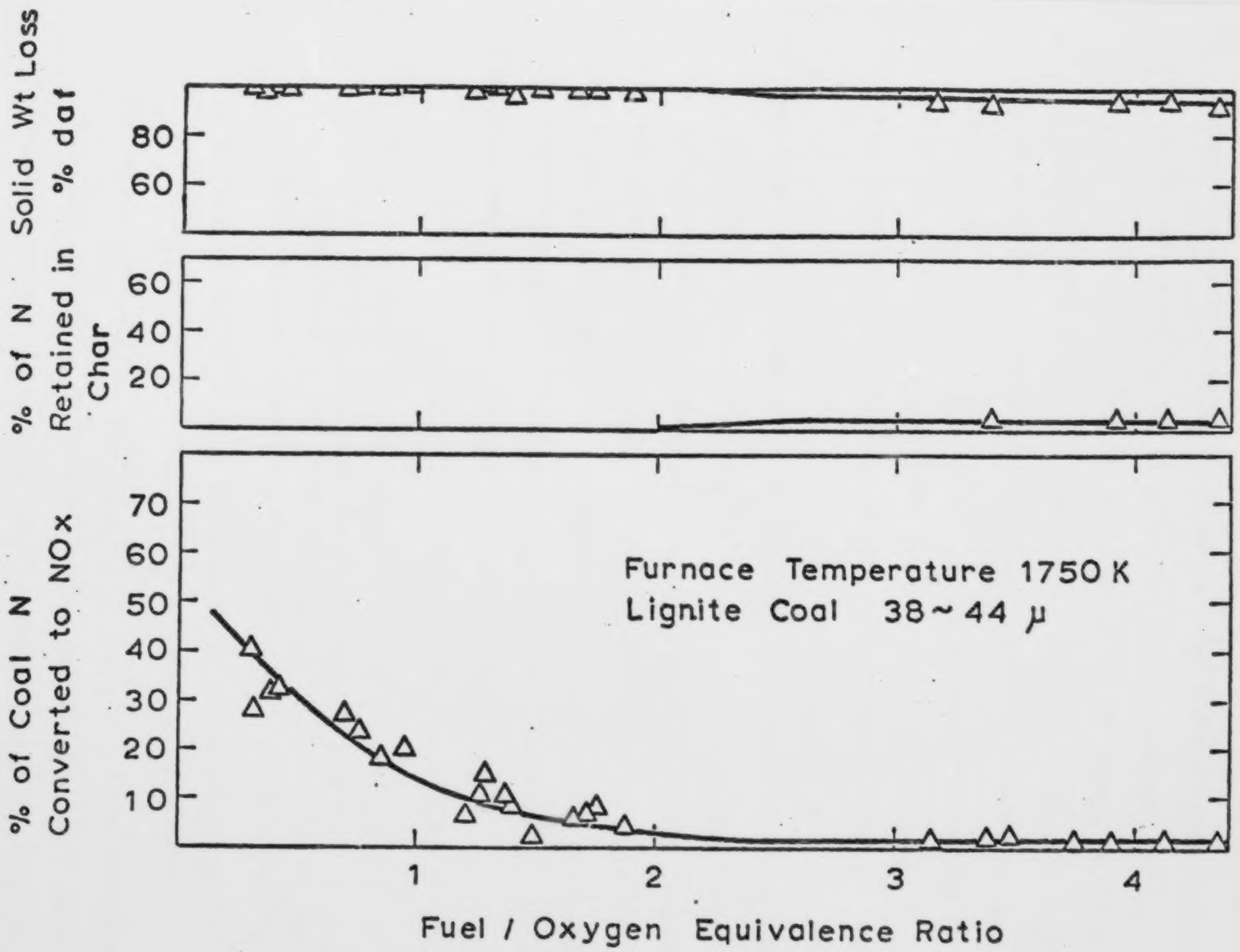


Figure V-10. Fate of Fuel Nitrogen During Oxidation: Conversion to Nitric Oxide (Bottom), Retention by Unburned Char (Middle), and Combustion Efficiency Defined by Solid Weight Loss (Top). Montana Lignite at 1750 K.

Similar conversion of lignite in a 1250°K furnace is shown in Figure V-11. Burnout, of course, is less efficient at the lower temperature. Conversion efficiency of fuel nitrogen to nitrogen oxides is, however, quite similar to that at 1500°K.

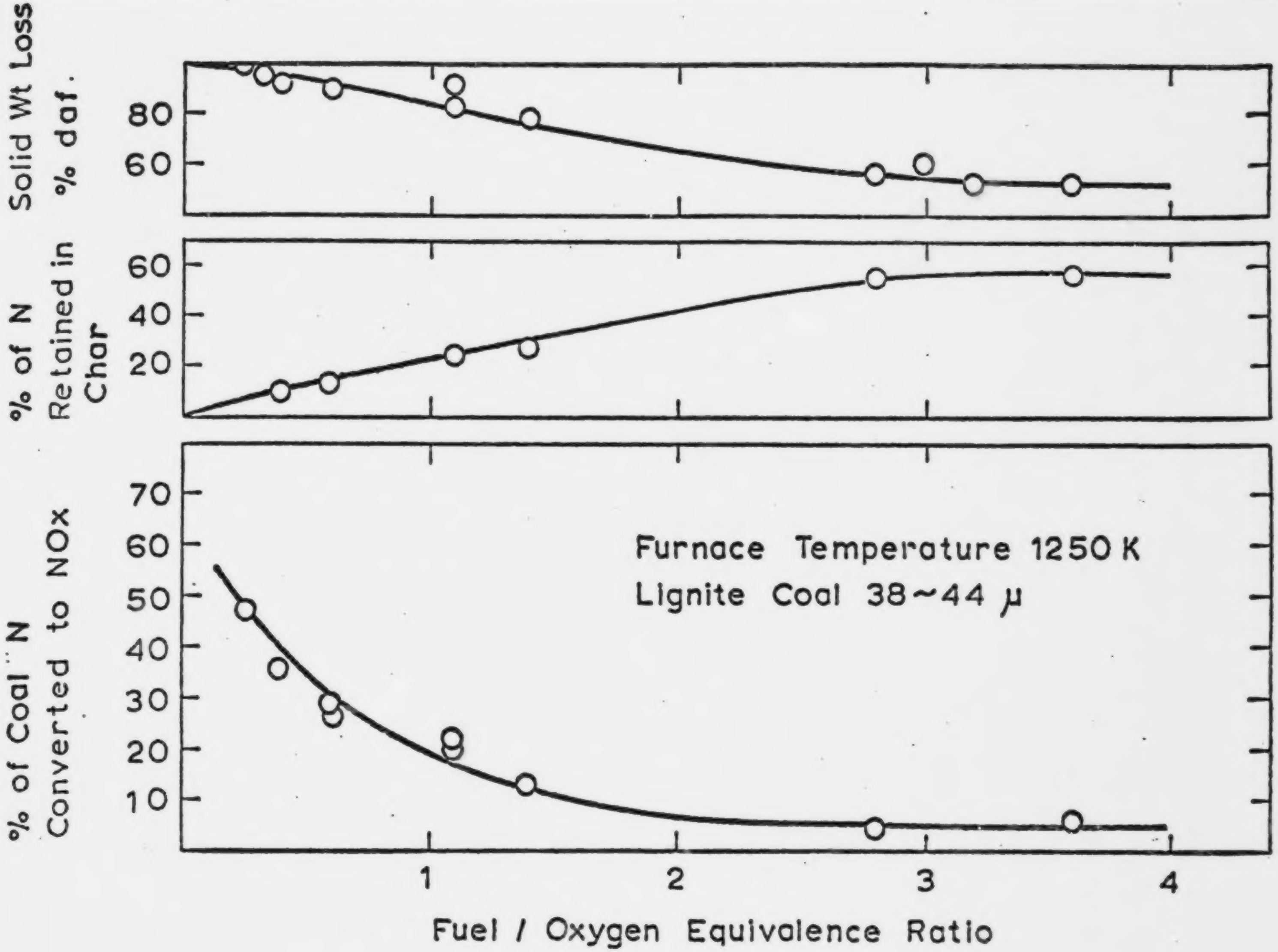


Figure V-11. Fate of Fuel Nitrogen During Oxidation: Conversion to Nitric Oxide (Bottom), Retention by Unburned Char (Middle), and Combustion Efficiency Defined by Solid Weight Loss (Top). Montana Lignite at 1250 K.

V-3.2 OXIDATION OF LIGNITE CHAR- FIXED RESIDENCE TIME

Lignite coal was devolatilized at 1500°K for one second and then oxidized in a 1500°K furnace supplied with varying amounts of oxidizer. Char produced in this manner has about 47% (d.a.f.) weight loss and 0.67% nitrogen. The results are shown in Figure V-12 and show similar trends, but with some differences, to oxidation of the raw coal. Asymptotic burnout in one second was not apparent for oxidation of char as it was for oxidation of coal at the highest fuel equivalence ratio of 2.6. This may result because the char has already been devolatilized at 1500°K and has very little volatile matter left to lose. For the case of raw coal, however, about 50 percent of the initial weight may be lost by pyrolysis in addition to any oxidation that occurs.

The nitrogen retained in the char is higher than that found for raw coals but there is more char remaining at a given condition. The fractional retention of the nitrogen in the char is expected to increase as the fuel equivalence ratio is increased, with a consequent increase in the amount of residual char.

The conversion of char nitrogen to nitrogen oxides follows a trend similar to the one observed for oxidation of raw coals. One striking difference between the conversion of coal nitrogen from chars and from coals is that the conversion for chars is significantly lower. Under fuel-rich conditions, the conversion of the nitrogen in the char reaches an asymptotic value of about 4% but about 50% of the nitrogen is retained in the solid residual, whereas at the same conditions, the conversion of the nitrogen in the raw coal is about 15% and the nitrogen retained in the char from the

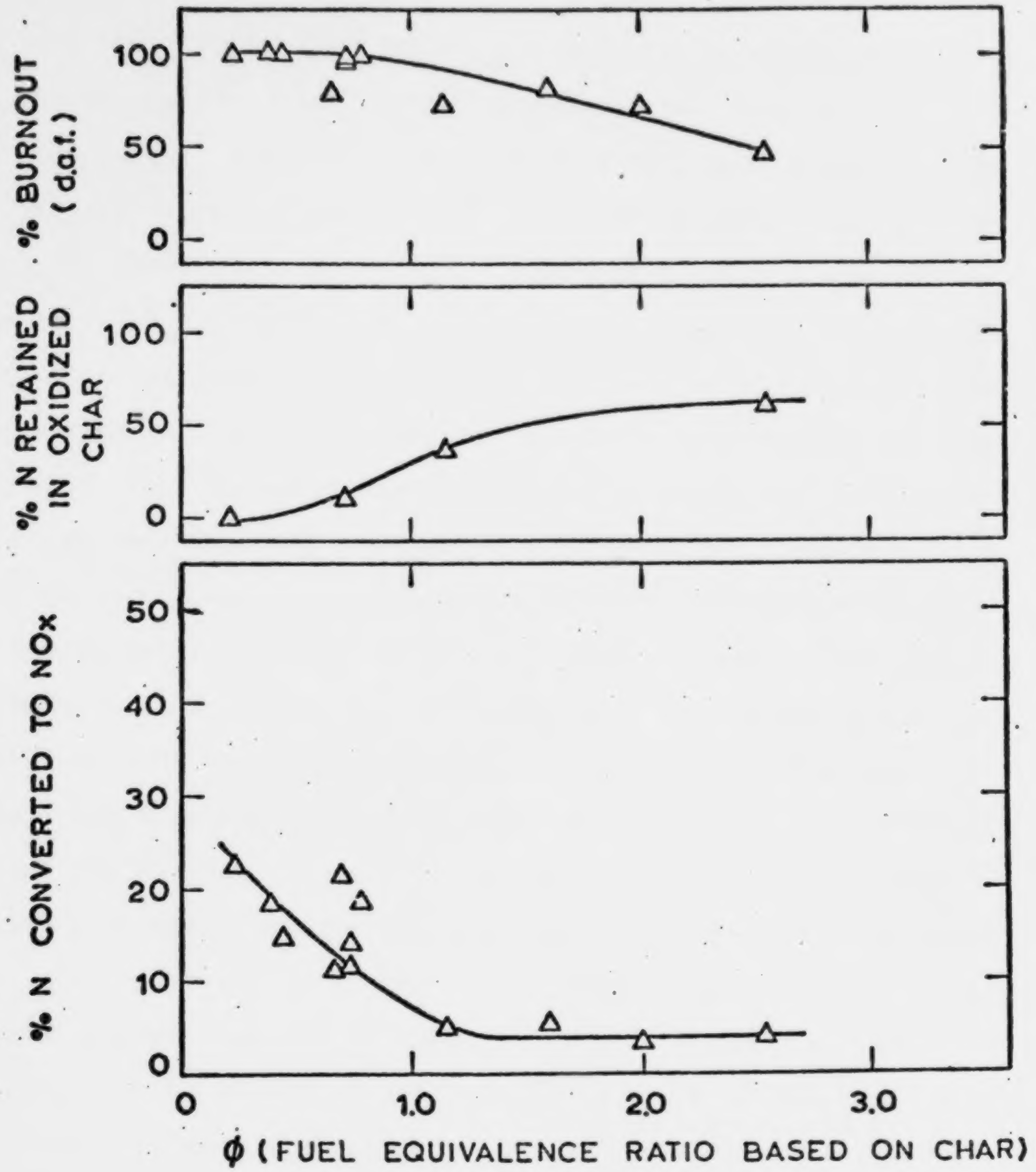


FIGURE V-12. Conversion of nitrogen vs fuel equivalence ratio in a 1500°K furnace for a lignite char previously devolatilized at 1500°K for 1 second.

coal is about 36%.

The residual unburned material from char oxidation is greater than from coal oxidation at similar conditions and the nitrogen retention of the residual from the char is correspondingly higher. However, even under conditions where no residual is left for either char or coal oxidation, the conversion efficiency of the char is significantly lower than that for the raw coal.

Similar results are obtained for oxidation of chars at two other temperatures. A lignite coal was devolatilized for one second at 1750°K and then oxidized in a 1750°K furnace. The results are shown in Figure V-13. Similarly, a lignite coal was devolatilized for one second at 1250°K and then oxidized in a 1250°K furnace. These results are shown in Figure V-14.

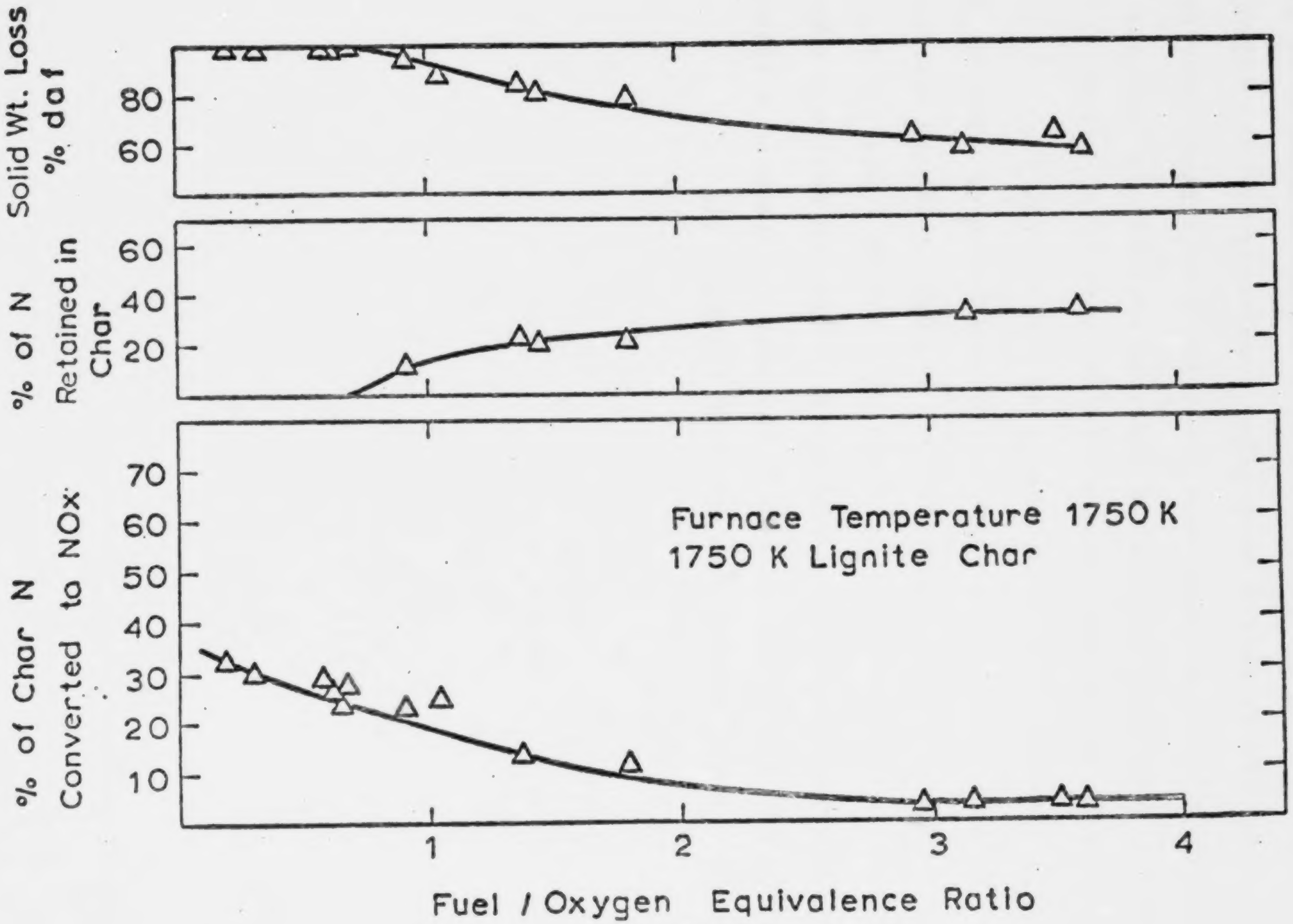


Figure V-13.

Fate of Char Nitrogen During Oxidation: Conversion to Nitric Oxide (Bottom): Retention by Unburned Char (Middle); and Combustion Efficiency (Top). Char from Montana Lignite Pyrolyzed and Oxidized at 1750 K.

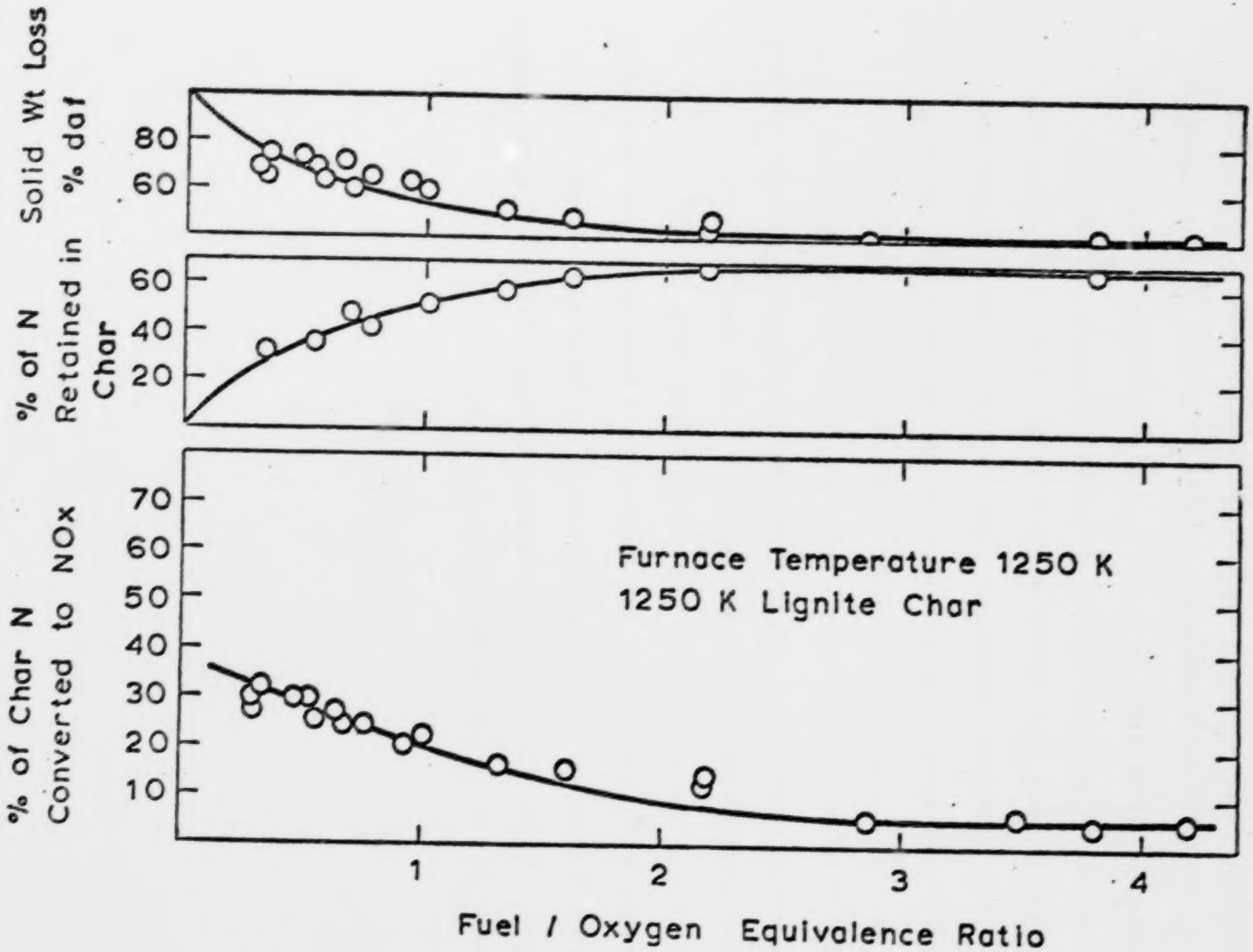


Figure V-14.

Fate of Char Nitrogen During Oxidation: Conversion to Nitric Oxide (Bottom); Retention by Unburned Char (Middle); and Combustion Efficiency (Top). Char from Montana Lignite Pyrolyzed and Oxidized at 1250 K.

V-3.3 OXIDATION OF SUB-BITUMINOUS COAL

FIXED RESIDENCE TIME- EFFECT OF TEMPERATURE

In an attempt to elucidate the effect of furnace temperature on the conversion of fuel-nitrogen to NO_x, an additional series of experiments were performed in the flow reactor. A Montana sub-bituminous coal in a 38-44 micron size cut was fed into the reactor for a 1 second residence time at three temperatures and a series of fuel/oxygen equivalence ratios varying from about 0.8 to 1.2. The results are shown in Figure V-15. Consistent with results of Section V-3.1, it can be seen that conversion efficiency increases with decreasing fuel/oxygen equivalence ratios at a fixed temperature. Similarly, at a fixed fuel/oxygen equivalence ratio, increasing the temperature from 1250°K to 1500°K renders little change in conversion efficiency, but a further temperature increase to 1750°K results in a decrease in conversion efficiency. A more detailed discussion of the effect of temperature on NO_x production is presented in Section VI.

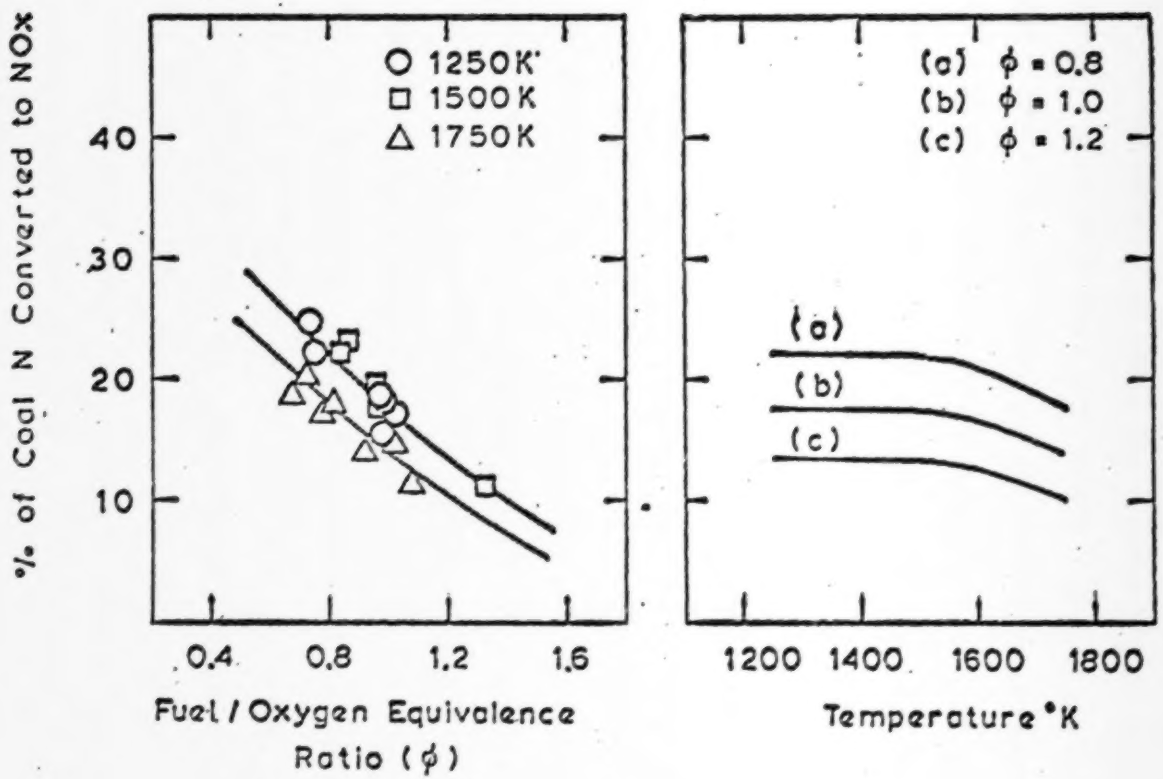


Figure V-15.

Effect of Temperature on Conversion of Coal Nitrogen to Nitric Oxide. Montana Sub-bituminous Coal.

V-3.4 TIME-RESOLVED OXIDATION OF CHAR

As can be seen from Figures V-10 and V-11, with increasing fuel/oxygen equivalence ratio, the percent conversion of coal nitrogen to NO_x decreases. Under the same fuel-rich conditions, however, an increasing amount of the coal nitrogen may escape the first stage of a staged combustor with the unburned char. The kinetics of char oxidation have, therefore, been investigated in order to establish residence time requirements for completion of the char combustion and to determine the fate of the char-nitrogen during oxidation.

A lignite char was prepared by feeding the lignite coal into a 1750°K furnace for a residence time of one second. The char, so prepared, was then fed into the furnace at temperatures of 1250°K, 1500°K, and 1750°K. Total weight loss and nitrogen and carbon elemental weight losses were then measured for two different oxygen partial pressures, and for residence times varying from about 200 milliseconds to about 600 milliseconds by positioning the collector probe at varying positions relative to the feeder according to the procedure outlined in Section III-2. The data are shown in Figures V-16 and V-17. As can readily be seen, total weight losses and initial weight loss rates increase with temperature and oxygen concentration. Nitrogen to carbon ratios, similarly, remain essentially unchanged or decrease only slightly with time at the lowest temperatures, but decrease significantly with increasing temperature. The decrease in N/C ratio is more pronounced at lower oxygen concentrations. These data are consistent with the contention that nitrogen is removed from the char both by

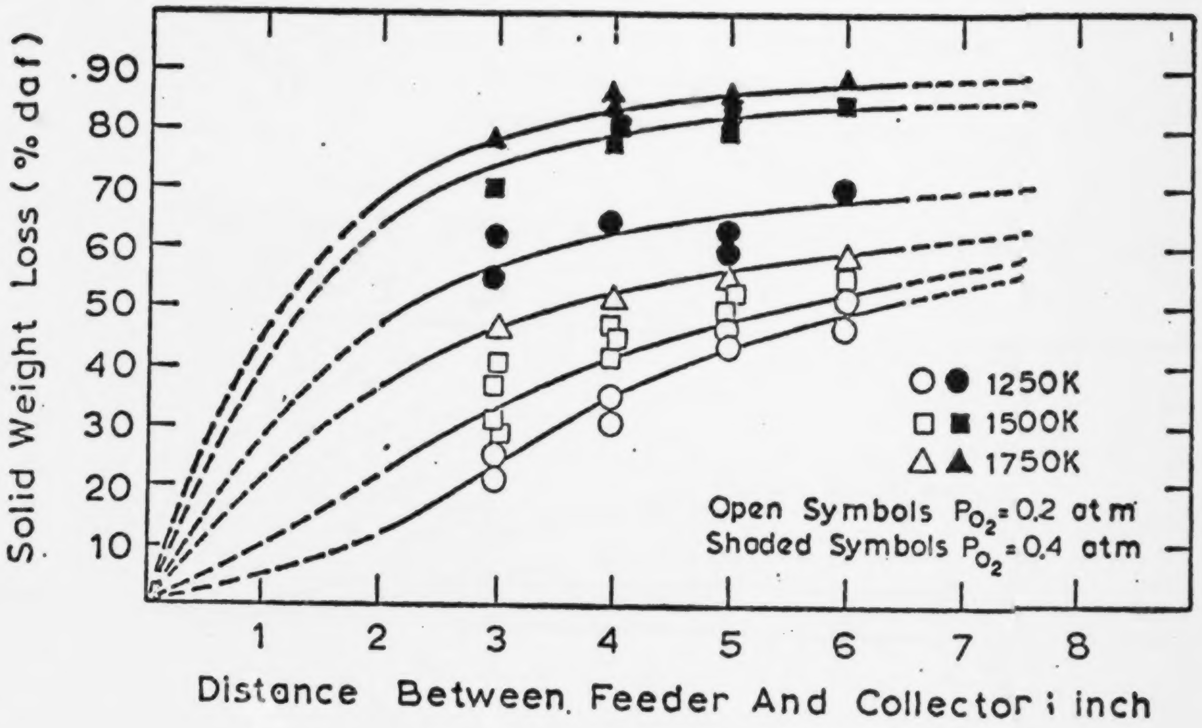


Figure V-16.

Weight Loss of Char Prepared from a Montana Lignite as a Function of Distance to the Collector During Oxidation.

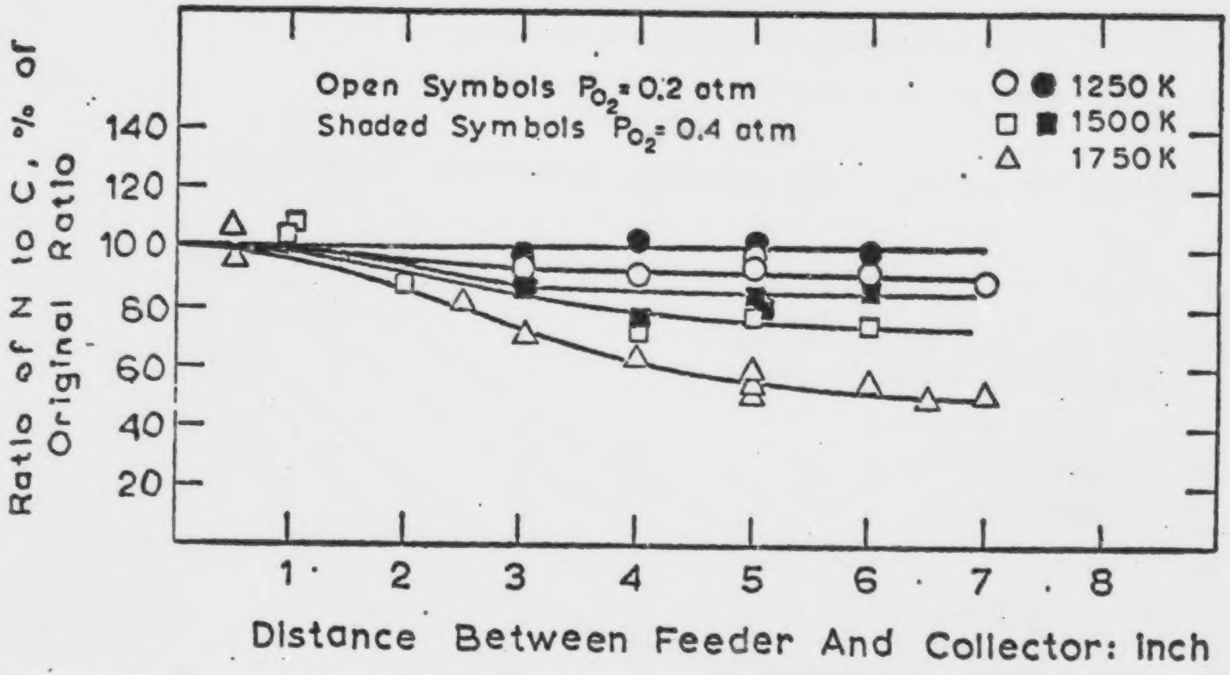


Figure V-17.

Nitrogen/Carbon Ratio as Percentage of that in the Original Char as a Function of Distance to the Collector During Oxidation.

continued devolatilization and heterogeneous oxidation, whereas carbon, thought to form more stable structures in the char, is further removed only by oxidative attack.

SECTION VI

DISCUSSION OF EXPERIMENTAL RESULTS

VI-1.0 DEVOLATILIZATION RESULTS

At the start of this period, no data existed in the open literature on devolatilization of nitrogen from coal at conditions applicable to pulverized coal flames. A relatively large body of data is available on nitrogen behavior in coal subjected to coking conditions, i.e. low temperatures, 950°C; slow heating rates, °C/min.; and in packed beds (Konle, 1928, Fielder and Davis, 1934, Davis and Parry, 1939, Kirner, 1947, Hill, 1945, Lowry, 1942, and Bronshtein, 1970). With the growth in interest in control of conversion of coal nitrogen to nitric oxide in pulverized coal flames, the data available on nitrogen behavior under coking conditions has been extrapolated to the conditions of pulverized coal flames and used to construct speculative models. Such extrapolations of coking data have led to misinterpretation of coal nitrogen behavior in pulverized coal flames.

Insofar as devolatilization can be viewed mechanistically as the first step in coal combustion (See, again, Section V-1.0), development of a strategy for control of NO_x emissions based upon combustion modification requires an accurate knowledge of the time/temperature history of devolatilization under conditions appropriate to pulverized coal combustion. Such experiments are also necessary for future development of a more detailed mechanistic model of coal pyrolysis which would hopefully relate evolution of volatile species to thermal rupture of specific bonds or functional groups in the complex matrix which comprises coal.

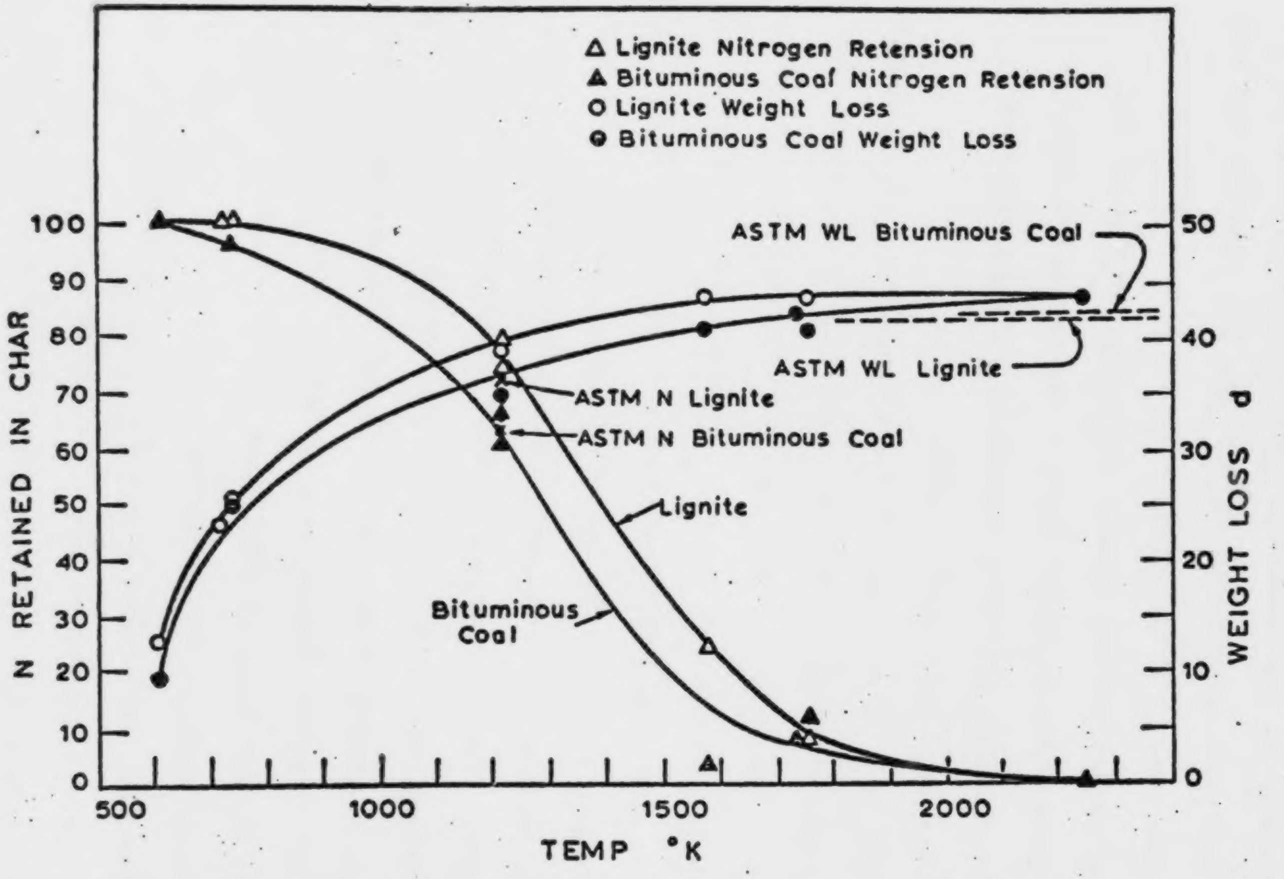
All of the pyrolysis data in this study were obtained from coal devolatilized in an inert atmosphere. In a real pulverized coal flame, of course, coal devolatilization occurs in a rich but not oxygen-free atmosphere. The pyrolysis data of this study were taken in an oxygen-free environment because the inert atmosphere allowed the effects of thermal decomposition to be clearly separated from the effects of oxidation. It is realized that thermal and oxidative pyrolysis, as well as oxidation, may not proceed by entirely independent mechanisms,but the experimental division outlined here represents the clearest, first-order approach to the problem. Future extensions of this work might involve a more detailed exploration of the coupling of the mechanisms of devolatilization and oxidation.

VI-1.1 ASYMPTOTIC CRUCIBLE RESULTS

Crucible results (Figures V-2 and V-3) in this study extended the maximum temperature of available data from about 1500°K to 2200°K. The nitrogen retention in the char and weight loss (dry basis) are shown versus maximum temperature in Figure VI-1. The nitrogen retention and weight loss are reported at the times at which weight loss approached an asymptotic value. Under conditions of asymptotic weight loss the chars may still undergo slow nitrogen loss.

In Figure VI-1, the low temperature portion of the nitrogen retention curve for lignite shows little nitrogen loss at temperatures below 750°K; for bituminous coal, 5% of the nitrogen is lost at the same temperature, even though the dry weight losses are about equal. In general, the nitrogen loss from the bituminous coal under coking conditions seems to be slightly greater than from the lignite. This slight difference might be explained by some small amount of the coal nitrogen being bonded in exinite resinous bodies that can distill without significant thermal degradation.

The retention of nitrogen in lignite and bituminous coal char is proportional to temperature between 80 and 20% retention in agreement with other data. The first and last portion of the nitrogen removal appears to be slower. The slow removal of nitrogen from coals implies that nitrogen is contained in coal in a relatively stable form, probably predominantly in heterocyclic nitrogen compounds.



Asymptotic Nitrogen Retension and Weight Loss Crucible Experiments

FIGURE VI-1. Coal nitrogen retention in the char under conditions of asymptotic weight loss.

Some of the data at 1223°K were obtained using the ASTM Proximate Analysis test and some were obtained by heating to the ASTM test temperature in the furnace. The nitrogen retention under ASTM Proximate Analysis conditions is 72% for the lignite and 63% for the bituminous coal. There appears to be little difference between nitrogen retention for either coal between actual and simulated ASTM Proximate Analysis tests. There was no obvious correlation between ASTM nitrogen retention and the nitrogen retention of chars in pulverized flames.

The nitrogen loss from both coals is complete at high temperatures. Very little nitrogen (less than 10%) is retained in the char at temperatures above 1750°K. Nitrogen is completely removed for both coals at a temperature of 2200°K, even though the weight loss is only 44% dry, and char has retained about 70-75% of the original carbon. The carbon retained in the crucible experiments is much higher than the carbon retained under simulated pulverized coal flame conditions. The conclusion is that under slow heating in packed beds, carbon can form complexes that are stable to at least 2200°K but that nitrogen compounds which may form higher molecular weight complexes are not stable at pulverized coal flame conditions.

The total weight loss at 2200°K is only marginally greater than the ASTM volatile matter, 44% compared to 42% dry. The ASTM volatile levels indicated by the dashed lines are well established by repeated tests from different laboratories. The weight loss shown at 1223°K, the ASTM temperature, was slightly lower for both lignite and bituminous coal but the difference is not thought to be significant.

VI-1.2 TIME-RESOLVED FLOW FURNACE RESULTS

The pyrolysis results of greatest interest for purposes of developing emission control strategies are those obtained under conditions most nearly approximating those found in pulverized coal combustors, namely, high heating rates, 10^4-10^5°C/sec, and high temperatures, 1500-2200°K. It is expected that high heating rates will result in weight losses differing somewhat from those found in the crucible experiments. As will be seen in a later section, these pyrolysis data are necessary for elucidating the mechanism of NO formation during coal burnout, in particular, for distinquishing NO formed through homogeneous gas phase oxidation from that formed via heterogeneous burnout of char. This matter is returned to in detail in Section VI-3. Since the amount of nitrogen devolatilized from coal under different conditions may have a large effect on control strategies, it is desirable, as indicated above, to develop a predictive model for nitrogen pyrolysis from coal that will be applicable to conditions in a pulverized coal flame.

Empirical models can be developed that adequately represent pyrolysis data. Little physical significance can, however, be ascribed to these models nor can they reliably be extended beyond the range of experimental conditions employed or coals studied. This, of course, severly limits the usefulness of these models. However, where fundamental models are difficult to develop, empirical relations do, often, serve useful engineering functions.

Coal pyrolysis has, in the past, generally been considered too complicated to model except empirically. New information developed, however, on the chemical and physical structure of coal does allow some physically realistic models of complex coal processes to be proposed. While the pyrolysis results presented here do lead to some conclusions concerning the nature of devolatilization and condensation reactions likely to predominate in coal pyrolysis, proposal of a full mechanistic pyrolysis model is considered beyond the scope of this work and will not, therefore, be attempted. We do, however, in the tradition of coal kineticists, present an empirical interpretation of coal nitrogen pyrolysis.

The usual first order treatment of nitrogen pyrolysis from coal, except that the rate is restricted to the first 10% of nitrogen loss, is compared with fundamental first-order rate constants in Figure VI-2. The rate constants were taken from a compilation by Benson and O'Neal (1970) and represent reliable experimental values which have been heavily weighted by absolute rate theory considerations. Also shown on the plot are some pyrolysis data taken on nitrogen compounds that might be considered to represent the form of fossil fuel nitrogen. The nitrogen compound pyrolysis data was taken from Hurd and Simon (1962) and Axworthy (1975).

The pseudo-first order rate constant derived from the initial slopes of the data presented in Figure VI-2 yields a value of

$$k_N = 9.3 \times 10^3 \exp(-22{,}700/RT) \text{ sec}^{-1}$$

for the Montana lignite-A and Pittsburgh Seam #8 hy-A bituminous coals studied here. It is apparent that the rate constant derived in this study does not resemble elementary first order reaction

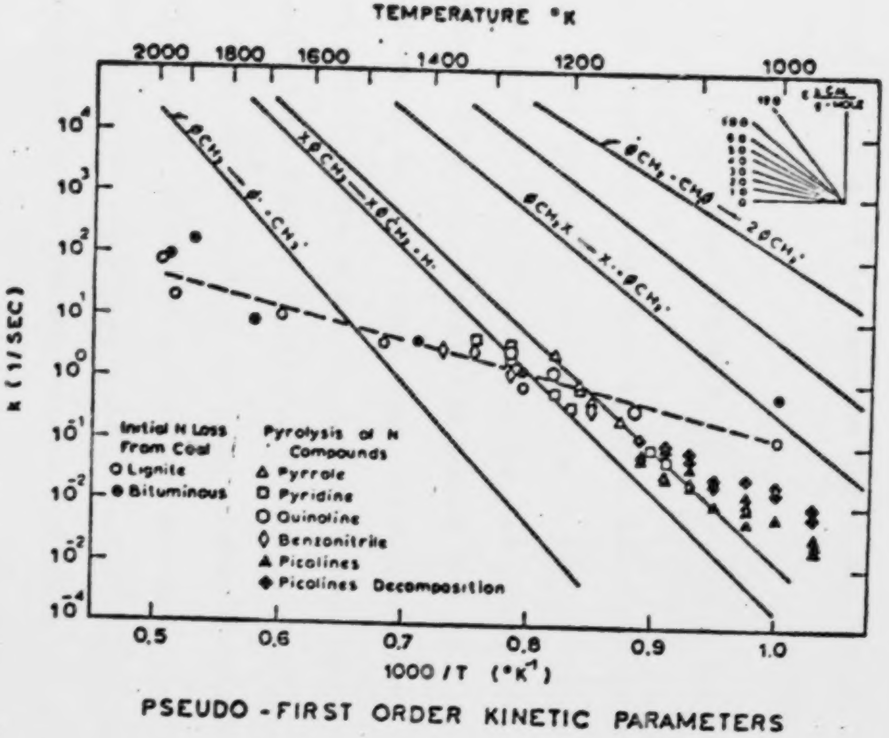


FIGURE VI-2. Comparison of rate of nitrogen removal from coal with pyrolysis of model nitrogen compounds and fundamental rate constants.

rate constants. Rate constants derived from pyrolysis of model nitrogen compounds are reasonably in agreement with the rate constants derived for nitrogen removal from the coals of this study but are in poor agreement with fundamental first order rate constants.

Kobayashi (1976) has derived rate constants from the same data in a parallel study and found an overall weight loss constant for both coals of about:

$$k_W = 6.6 \times 10^4 \exp(-25{,}000/RT) \text{ sec}^{-1} .$$

The rate constants derived for loss of hydrogen, carbon, and oxygen were also very similar to the constants for nitrogen loss and overall weight loss. Kobayashi has tabulated previously derived coal pyrolysis rate constants and found the constants, within a range of scatter, to be consistent with each other and to be consistent with rate constants derived similarly in this study. The rate constants do not agree with the theoretical values that would be predicted if the kinetic models used to interpret the data were physically realistic. The conclusion to be drawn is that first order kinetic models can explain individual sets of data, provided enough parameters are used, but cannot predict consistent rate constants for coal pyrolysis.

It is probably obvious that coal pyrolysis involves an entire spectrum of reactions of different orders, including parallel, sequential, and competitive paths. As pyrolysis is traditionally interpreted as occurring in a single reaction which is first order in material remaining to be reacted, it is not surprising that rate parameters so derived do not resemble rate constants for elementary reactions. It is extremely difficult, therefore, to derive physically meaningful pyrolysis rate parameters for a substance as complicated as coal.

Perhaps a more useful analysis of the coal pyrolysis data, from the viewpoint of development of a mechanistic model, is the correlation of elemental nitrogen loss with total volatile loss under conditions applicable to pulverized coal flames. This is demonstrated in Figure VI-3.

The rate of nitrogen loss during pyrolysis is not independent of the loss of other elements during pyrolysis because C, H, O, N, and part of the S are bonded together in intricate chemical structures. Kobayashi (1976) has demonstrated the similarity between individual element removal rates and the rate of total weight loss Gray, _et_ _al_ (1975) have also produced empirical correlations between the extents of various element loss during hydrogasification of coal.

Figure VI-3 shows nitrogen retention versus d.a.f. weight loss for the two coals of this study subjected to pyrolysis in flow experiments (open points), free fall into crucible (half-open points), and crucible results (solid points). The correlation between nitrogen loss and total weight loss is good for both coals when only the laminar flow data is considered. The data for pyrolysis of the coals in crucibles show a much higher rate of nitrogen loss than carbon loss.

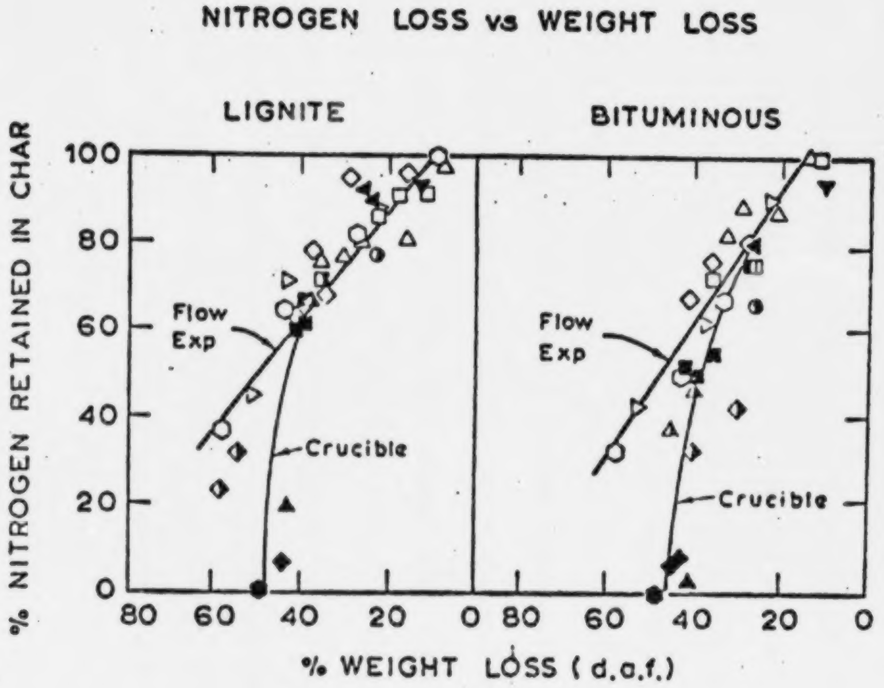


FIGURE VI-3. Correlation between nitrogen loss and total weight loss during pyrolysis of coal.

In the long residence time crucible experiments reported in Section V-2.1 it was demonstrated that the total weight loss reached an asymptotic value only slightly higher than would be predicted by the ASTM Proximate Matter Test, but that elements other than carbon were completely removed. This can be explained because carbon is the only element that can form a highly condensed substance that is stable at pulverized coal flame temperatures. Nitrogen is not thought to have sufficient bonding electrons to participate in high order condensation reactions with carbon. Nitrogen must, therefore, be present only on the periphery of the char structure where it can be removed under the conditions of a pulverized coal flame.

Gray, et al. (1975) observed similar behavior in his experiments on hydrogasification of coal. Under conditions similar to those used in this work Gray found that nitrogen loss and carbon loss were related linearly with a slope of 1.8. However, when coal was pyrolysized in his "hot rod" reactor with heating rates and environmental conditions more nearly like those encountered in the crucible experiments of this experiment, nitrogen loss was no longer linearly related to carbon loss. Nitrogen loss was more rapid than carbon loss and nitrogen could be completely removed with removal of as little as 30% of the carbon.

Nitrogen loss does not commence with carbon loss but is delayed until approximately 10-20% of the carbon is lost. This is consistent with the belief that some of the carbon is contained in alphatic structures that are easy to remove compared to destruction of aromatic stuctures, while most of the nitrogen is probably held in heterocyclic ring stuctures.

Nitrogen is removed from coal more rapidly than total weight loss occurs, after the initial delay in nitrogen removal, as in evidence from the slope of the curves; the ratio of nitrogen loss versus weight loss is 1.25 for the lignite and 1.5 for the bituminous coal.

Nitrogen loss from different coals at pulverized coal flame conditions in an inert atmosphere can then be crudely estimated, probably within 10 to 20 percent, from total weight loss data by use of the shape and nature of Figure VI-3. No nitrogen loss should be assumed until approximately 15% of the total weight has been lost, then nitrogen loss can be estimated as approximately 1.25-1.5 times the total weight loss until approximately 60% d.a.f. weight loss has occurred. Extrapolation of this relationship beyond 60% weight loss is uncertain and would predict that, for pyrolysis of coals under inert pulverized coal flame conditions, complete nitrogen loss will occur at 80-90% total weight loss.

VI-1.3 PRIMARY NITROGENEOUS PYROLYSIS PRODUCTS

It is possible at this juncture to draw some educated conclusions as to the primary fate of fuel-nitrogen released as volatiles from coal.

Pyrolysis data of this study indicates an induction period after heating prior to release of fuel nitrogen from coal. This is though to reflect the common speculation that most of the fuel nitrogen is contained in reasonably stable, heterocyclic structures, rather than in labile side chains. Consistent with this belief is the recent observation of Blair, et al (1976) that under pyrolysis conditions most of the coal nitrogen is, in fact, evolved as tars and heavy, hetrocyclic molecules. These large molecules are then thought to undergo secondary pyrolysis to yield HCN as the major nitrogen-bearing species. Studies by Axworthy (1976) on the pyrolysis of model compounds indicate rapid rates for this pyrolysis step which, when extraplated to temperatures pertinent to pulverized coal combustion, suggest that formation of HCN from these heavier molecules is very rapid and certainly not rate controlling.

The results of this study seem to confirm this mechanism; closure of the nitrogen material balance at high temperatures (See Section V-2.3) resulting in HCN and N_2 showing up as the major stable species. The N_2 so observed, however, is almost certainly a product of the secondary pyrolysis of HCN, and not a primary pyrolysis product. This is easily understood from the complementary observation that under fuel-lean, low-temperature conditions (See Figure VI-4), conversion of volatile fuel-nitrogen to NO_x is essentially complete. Insofar as, under these conditions, N_2 is not thought to be a reasonable precursor to NO, N_2 cnnot be a primary pyrolysis product of coal.

VI-2.0 OXIDATIVE RESULTS

The primary objective of this work is the elucidation of the mechanism of NO_x formation during pulverized coal combustion with a specific view towards development of a strategy for the minimization of NO_x emissions. As will be seen, NO_x can originate both from gas phase oxidation of nitrogen bearing volatiles emitted from the initial pyrolysis of the rapidly heated coal as well as from heterogeneous oxidation of the devolatilized char. Insofar as the chemical mechanisms of these two processes are rather different, variation of combustion conditions by the standard techniques available to the combustion engineer, e.g. change of temperature, fuel/air equivalence ratio, degree of mixedness, staging of combustion, etc., may effect the two processes quite differently; and it is certainly not immediately obvious what combinations of combustion conditions will lead to a minimum in NO_x emissions. In an attempt to gather at least an empirical understanding of the factors affecting the split of fuel-nitrogen between volatiles and char and the oxidation of each, a series of independent coal and char burnout experiments were undertaken. These results, combined with the pyrolysis data of the previous section, will be seen to throw valuable light on the problem.

All experiments were run in the laminar flow reactor described above in Section III. As such, aerodynamic conditions were not varied. In a somewhat parallel study, however, Pershing and Wendt (1976) investigated the effect of mixing in a 6 lb/hr unit and found that efficiency of fuel nitrogen conversion to nitric oxide was affected by burner aerodynamics but not affected by flame temperature, provided the flame temperature was not too high. The results of Pershing and Wendt on fuel nitrogen conversion on a similar coal agree with the conversions of this study. For instance, at 15% excess air a Pittsburgh coal with 1.20% nitrogen showed about 28% conversion; approximately the same value was obtained for a similar coal in this study.

Pershing and Wendt injected coal through a divergent nozzle and an axial injector and found, when everything else was equal, about a 10% absolute difference in conversion efficiency between the two nozzles for a Western Kentucky hvC bituminous coal and Montana sub-bC coal. The injector system used in this study is close to the axial injector system used by Pershing and Wendt. The burner design had no effect on char oxidation. The injector used in this study can not match the mixing conditions encountered in a pulverized coal flame and so represents a different flame. Data, however, can be compared on a relative basis for this mixing condition and valid conclusions can be drawn about the effects of variables other than mixing for systems in general.

Pershing and Wendt used adiabatic flame temperatures as a comparison of temperature effects on fuel nitrogen behavior since they had no direct measure of the flame temperature. Comparison of the effects of flame temperatures on thermal and fuel nitrogen emission showed that thermal nitric oxide emissions increased greatly at higher temperatures but fuel nitrogen conversion did not increase until the adiabatic flame temperature reached about 2400°K. The stoichiometric adiabatic flame temperatures in helium for the coals of this study, disregarding dissociation, were about

2100°K for the lignite and about 3000°K for the bituminous coal; corrections for dissociation will lower the lignite temperature about 200°K and the bituminous coal 300°K.

VI-2.1 COAL OXIDATION

In this study, coal particles, nominally in the size range of 38-45 microns, or, occasionally, 75-90, were injected with an equal mass of gas through a 1-2 mm nozzle into a hot wall furnace. Oxygen content of the helium/oxygen carrier stream corresponded to 15-25% of the stoichiometric requirement which corresponds well with the values of the primary air utilized in industrial practice. The secondary air (again stimulated by a helium/oxygen mixture) was injected through a honeycomb flow straightener surrounding the coal-feed nozzle. In view of the difference between the mode of operation in this study and practical systems, the gross agreement in the data is remarkable. The conversion of fuel nitrogen to nitric oxide in our system for a fuel equivalence ratio of 0.7 is about 30 percent which is towards the upper end of the range of estimates for field units.

Comparison of the results in Figures V-9 and V-10 suggest that higher temperatures appear to have lower fuel nitrogen conversions. At a normal operating fuel equivalence ratio of 0.7, the percentage of fuel nitrogen conversion to nitric oxide decreased by several percentage points absolute when the furnace temperature was increased from 1500 to 1750°K. At the higher temperature, as would be expected, the burnout was markedly improved and the amount of nitrogen retained in the char drastically reduced.

Because the data of Figures V-9 and V-10 were gathered over a long time span, and because of the current interest in the effect of temperature on NO_x emissions from pulverized coal flames, the effects of temperature were rechecked in an independent series of experiments using a Montana sub-bituminous coal. These results, shown in Figure V-15, confirm the tendency towards decreasing conversion efficiencies with increasing temperature. The effect of temperature on controlling NO_x emissions is returned to in Section VI-3.

VI-2.2 CHAR OXIDATION

Essential to elucidating the mechanism of fuel nitrogen conversion to NO_x is an understanding of the split of fuel nitrogen between volatiles which are homogeneously oxidized to NO_x and char which is heterogeneously oxidized. Such information can be gleaned from a comparison of coal oxidation results, which, inherently, include contributions from both processes and char oxidation results, which, necessarily, involve only the latter process.

The conversion efficiency of fuel nitrogen to nitric oxide for a char was lower by about 10% absolute than the corresponding value for a coal at a fuel equivalence ratio of 0.7. The effect of fuel/oxygen ratio on conversion of the fuel nitrogen to nitric oxide in the coal was similar to that for the char (See Figures V-9 through V-14). The fractional burnout of the char was lower than the corresponding values for coal at fuel rich equivalence ratios. In addition, more nitrogen was retained by the unburned char than the unburned coal.

Pershing and Wendt (1976) report values for the conversion efficiency of the nitrogen in a char of about 13 percent at a fuel equivalence ratio of 0.7 for both a divergent nozzle and an axial injector. This conversion efficiency agrees well with the value found in this study using a char devolatilized at 1500°K for one second. It seems reasonable that mixing should have much less effect on the slow heterogeneous oxidation reactions than on the oxidation of volatiles.

Figures V-9 through V-11 demonstrate that with increasing fuel equivalence ratios, the percent conversion of coal nitrogen to nitric oxide decreases. Under the same fuel rich conditions, however, an increasing amount of the coal nitrogen may escape the first stage of the combustor with the unburned char. The study of the kinetics of oxidation of char was therefore undertaken with the objective of establishing the residence time requirements for completing the combustion of the char and determining the fate of the char-nitrogen during oxidation. The data in Figures V-16 and V-17 are plotted as a function of distance. For determining kinetic parameters, residence time measurements are necessary. Such measurements were made by Kobayashi (1976) who used essentially the same system and showed that the average particle velocity may be approximated by 1.4 times the average main gas velocity. For the interpretation of results of the present study, distances were converted to residence times, using Kobayashi's approximation. The results with times reported in milliseconds are summarized below:

Distance, inch					
Temperature, K	3	4	5	6	7
1250	256	340	427	512	599
1500	213	283	356	426	500
1750	183	243	305	365	428

It has been previously shown (Figures V-4 and V-5) that during coal pyrolysis the carbon loss appears to become asymptotic at times exceeding 100 milliseconds at 1750°K, the temperature used to produce the char in this study, but that nitrogen release continues for longer times. The rationalization of the results was that while carbon is present in relatively stable compounds in the char, no comparable stabilized nitrogen structures are formed; consequently, char-nitrogen continues to be released until it is completely eliminated from char. Therefore, when a char particle is oxidized, the nitrogen loss will be due to both devolatilization and oxidation, but the carbon loss will be exclusively due to oxidation.

Assuming the fuel nitrogen is uniformly distributed throughout the char, the oxidation rate of the nitrogen should therefore equal the product of the oxidation rate of the carbon and the mole ratio of the fuel nitrogen to carbon in the char (Wendt and Schulze, 1976). Since the pyrolysis loss and oxidation loss of char-nitrogen are additive, the consumption rate of char-nitrogen can be written as:

$$\left\{\begin{matrix}\text{Total Consumption-Rate}\\ \text{of Char Nitrogen}\end{matrix}\right\} = \left(\begin{matrix}\text{Consumption-Rate of}\\ \text{Char-Nitrogen Due}\\ \text{to Pyrolysis}\end{matrix}\right) + \left(\begin{matrix}\text{Consumption-Rate of}\\ \text{Char-Nitrogen Due}\\ \text{to Oxidation}\end{matrix}\right)$$

OR

$$\frac{dN}{dT} = \left(\frac{\partial N}{\partial t}\right) \text{Pyrolysis} + \left(\frac{\partial N}{\partial t}\right) \text{Oxidation}$$

Since $$\frac{dC}{dt} = \left(\frac{dC}{dt}\right) \text{Oxidation}$$

Therefore,

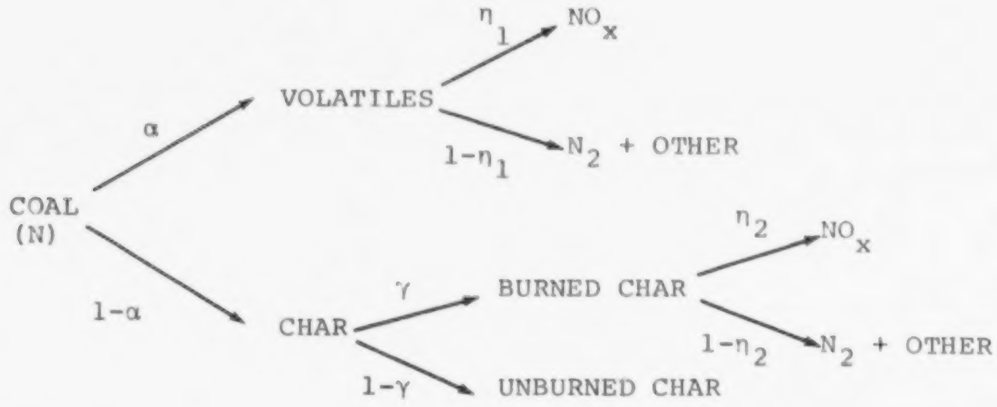
$$\frac{dN}{dt} = \left(\frac{\partial N}{\partial t}\right)_{\text{Pyrolysis}} + \left(\frac{dC}{dt}\right)_{\text{Oxidation}} \left(\frac{N}{C}\right)_{\text{Following Pyrolysis}}$$

This model indicates that for low oxygen pressure and high temperature char oxidation, the nitrogen to carbon ratio in the char will decrease as a function of reation time. As the oxygen pressure increases and temperature decreases, the oxidation process tends to dominate, resulting in a nitrogen/carbon ratio which is approximately constant during the course of the combustion process. The experimental findings support this conclusion. The data can be used to derive kinetic parameters for the oxidation and pyrolysis of the char nitrogen. The experiments were carried out with large excess of oxygen so as to maintain a constant oxygen partial pressure and thus facilitate interpretation of the results. The basic kinetic parameters derived from the data can be used to analyze char burnout under the varying oxygen concentrations that are encountered in practical combustors.

VI-3. THE CONTRIBUTIONS OF VOLATILE AND CHAR NITROGEN TO NITRIC OXIDE

Very little information exists on the contribution of nitric oxide produced from the oxidation of char and from the oxidation of volatiles. Pereria *et al* (1975) have shown the volatile contribution in a fluidized bed to be negligible at temperatures below 1000°K but to increase until the nitric oxide produced from volatile matter accounted for 2/3 of the total emission at 1200°K. These figures agree qualitatively with the results of this study, although the systems, temperatures, and mixing patterns must be considerably different.

The data from Figures V-9 through V-14 can be used to obtain preliminary estimates of the fractions of the NO_x formed in pulverized coal flames that are contributed by the volatiles and char. As a first order approximation it will be assumed that the conversion efficiencies to nitric oxide of the nitrogen in the char and volatiles are independent. The fate of the fuel nitrogen during combustion of coal can be represented by the following simplified scheme:


η_1
NO_x
VOLATILES
α
$1-\eta_1$
N_2 + OTHER
COAL (N)
η_2
NO_x
$1-\alpha$
γ
BURNED CHAR
CHAR
$1-\eta_2$
N_2 + OTHER
$1-\gamma$
UNBURNED CHAR

where

α = fraction of the coal-N that is released as volatiles
$1 - \alpha$ = fraction of the coal-N that is retained in the char
η_1 = fraction of the volatile-N that is converted to NO_x
γ = fraction of the char-N that is consumed
$\gamma\eta_2$ = fraction of the char-N that is converted to NO_x

The overall fractional conversion, η^*, of coal-nitrogen to nitric oxide is then:

$$\underbrace{\eta^*}_{\text{Overall Conversion to } NO_x} = \underbrace{\alpha\eta_1}_{\text{Volatile Combustion}} + \underbrace{(1 - \alpha)\,\gamma_{\eta_2}}_{\text{Char Contribution}}$$

The value of $(1 - \alpha)$ as a function of temperature is obtained from the pyrolysis data of Figure V-6. Values of η^* and $\gamma\eta_2$ as functions of temperature and fuel equivalence ratio are obtained from the coal oxidation data of Figures V-9 through V-11 and from the char oxidation data of Figures V-12 through V-14. From this information and the above scheme for fuel-nitrogen partitioning, it is possible to derive values for both the efficiency of volatile nitrogen conversion to NO_x, η_1, and the function of total NO_x contributed by volatiles $(\alpha\eta_1/\eta^*)$. These values are plotted as a function of fuel/oxygen equivalence ratio for the two temperature extremes of these experiments, 1250°K and 1750°K, in Figure VI-4. The efficiency of conversion to NO_x of nitrogenous species evolved as volatiles (η_1) and the fraction of overall conversion to NO_x which originates from

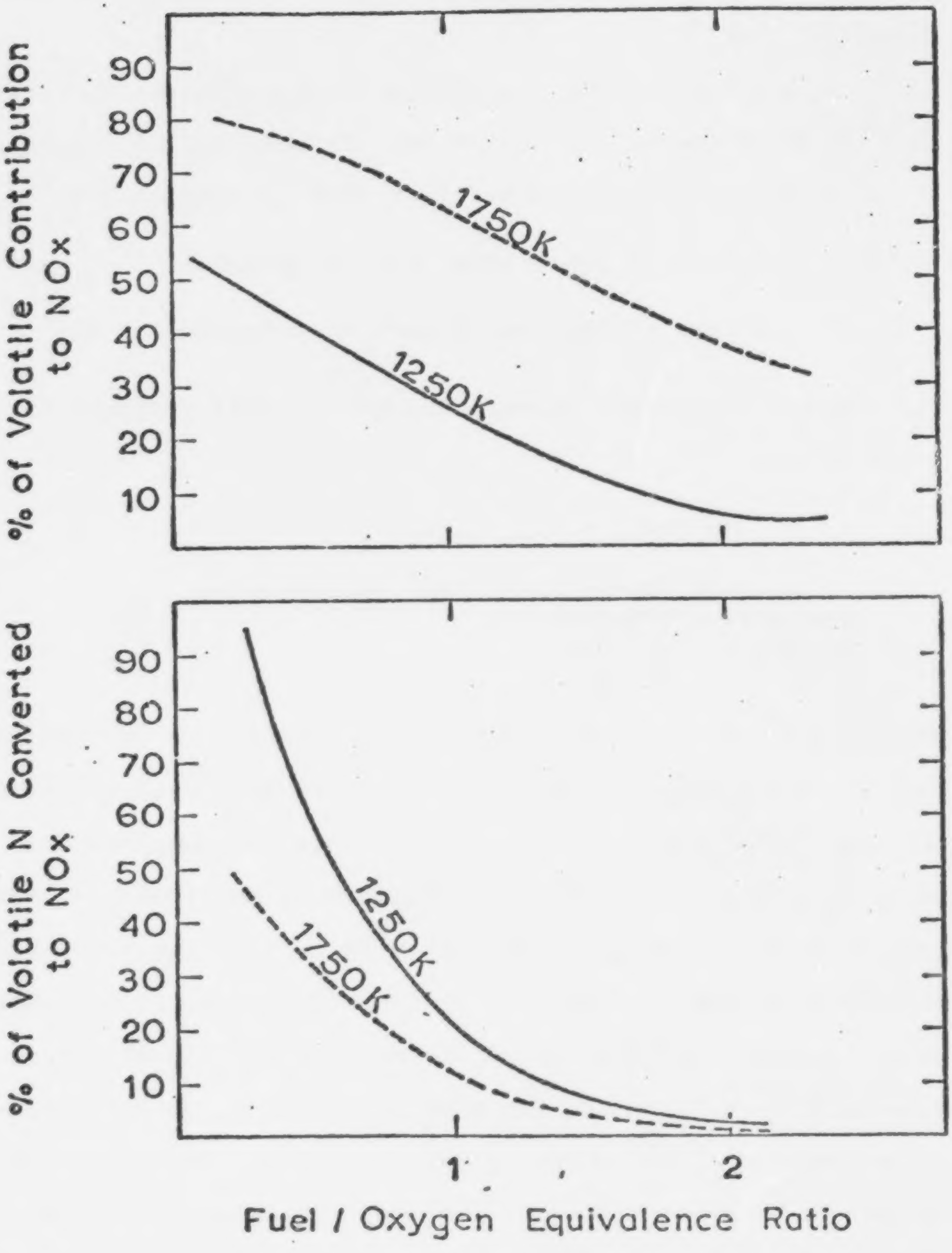


Figure VI-4.
Contribution of Volatiles to NO_x Emission:
Total NO_x Contributed by Volatiles (Top), and
Conversion of Volatiles to NO_x (Bottom).

volatiles $\left(\frac{\alpha\eta_1}{\eta^*}\right)$ are both seen to decrease monotonically with increasing fuel/oxygen equivalence ratio. The former result is entirely consistent with previously reported data on the conversion of volatile fuel-nitrogen to NO_x in both premixed (Fenimore 1972, Sarofim, *et al* 1975) and laminar diffusion flames (Sarofim, *et al* 1975) and, in fact, can be shown to fall between the two extremes. The latter result, however, would not have been obvious, *a priori*, and represents the fact that though char nitrogen conversion efficiency to NO_x also decreases with increasing fuel/oxygen equivalence ratio (See Figures V-13 and V-14), its rate of decrease is not as rapid as that of the volatiles.

Also of great interest is the effect of temperature on the volatile/char nitrogen partitioning and conversions to NO_x of fuel nitrogen. Comparison of Figures V-13 and V-14 for char oxidation at 1750°K and 1250°K suggests that the fractional conversion of char nitrogen to NO_x is independent of temperature. (The data of Figure V-12 at 1500°K, obtained much earlier in the studies, is thought to be of lower reliability and to exhibit more scatter.) The results of Figure VI-4, however, indicate that the fractional conversion to nitric oxide of the volatile nitrogen (η_1) decreases with increasing temperature. This result is consistent with the general observation that increases in fuel nitrogen concentration result in a decrease in conversion of fuel nitrogen to nitric oxide. As the temperature is increased, the fraction of the fuel nitrogen devolatilized increases and the concentration of fuel nitrogen in the gas phase must also increase. Interestingly, however, the results of

Figure VI-4 also indicate that with increasing temperature the fractional contribution to total NO_x by volatile $\left(\frac{\alpha\eta_1}{\eta^*}\right)$ increases. This, as inspection, again, of Figure V-6 reveals, is not inconsistent with the observations above in that with increasing temperature, a much larger fraction of the fuel nitrogen is evolved as volatiles. The results of Figure VI-4 merely imply that the rate of increase of volatile evolution with increasing temperature exceeds the complementary rate of decrease in conversion efficiency to NO_x. These two effects tend to compensate and partially explain the small dependence on temperature of the net conversion of coal nitrogen. In this study, a small net decrease is observed (See Figure V-15). In a separate study, Pershing (1976) has found practically no effect of temperature on the conversion of fuel nitrogen to nitric oxide.

VI-4. CONCLUSIONS AND IMPLICATIONS FOR CONTROL OF NO_x EMISSIONS

Major conclusions of this work may be summarized as follows:

(1) Evolution of nitrogen from coal is kinetically controlled for conditions encountered in typical pulverized coal flames. Although carbon forms a stable char through condensation reactions, no comparable stabilized nitrogen structures are formed. Consequently, nitrogen can be completely eliminated from the char at temperatures exceeding 1750°K.

(2) When coal is slowly heated under an inert atmosphere in a crucible, most of the volatile matter evolution occurs at temperatures below that of the ASTM Proximate Analysis test (1023°K), whereas most of the nitrogen is evolved at higher temperatures.

(3) The early stages of pyrolysis of nitrogen from coal can be empirically correlated, for the two coals studied, by a pseudo-first order rate constant of value:

$$k = 9.3 \times 10^{3} \; \text{[illegible]} -22,700/RT) \; \text{sec}^{-1}$$

(4) Little nitrogen is lost, under pyrolysis conditions, until 10-15% of the weight of the coal has been devolatilized. After this initial induction period, most likely associated with loss of side chains and scission of aliphatic bridges in coal, the rate of fractional nitrogen loss is found to be proportional to the rate

of fractional total weight loss.

(5) Conversion of fuel nitrogen to nitric oxide in pulverized coal flames decreases with increasing fuel/oxygen ratio, falling to negligible values at equivalence ratios greater than 1.5. However, at temperatures of 1500°K or lower, some of the coal persists as unburned char which may contain a significant fraction of the original fuel nitrogen.

(6) Conversions to nitric oxide of fuel nitrogen during char burnout are 2-3 times lower than the corresponding values for coal.

(7) During coal burnout, fuel nitrogen is partitioned between volatiles and char, higher temperatures favoring a larger fraction of volatiles. The efficiency of conversion of the volatile nitrogen to nitric oxide decreases with increasing fuel/oxygen ratio and decreasing flame temperature. The efficiency of conversion of char nitrogen to nitric oxide also decreases with increasing fuel/oxygen ratio, albeit, more slowly than does volatile nitrogen, but is, however, rather insensitive to temperature. Carbon burnout, of course, is enhanced at higher temperatures.

(8) Oxidation experiments on chars support the view that there is no selectivity between nitrogen and carbon loss during oxidation but that the char

nitrogen may undergo further pyrolysis in parallel with the oxidation.

The above results may be used to guide the development of control strategies. In a single stage combustor, conversion of nitrogen to nitric oxide may be reduced by the increase in the fuel/air ratio, to the limit imposed by the emission of unburned carbon, CO, or soot. Because of the compensating effects discussed above, little change in fuel nitrogen conversion to nitric oxide can be expected with changes in combustion temperature but the contribution of thermal fixation of nitrogen will decrease with decreases in combustion temperature.

In a staged combustor, the conversion of fuel nitrogen to nitric oxide can be decreased by increasing the fuel/air ratio, which results in decreases in conversion efficiency of the fuel nitrogen to nitric oxide for the nitrogen content of both volatiles and char. Since char oxidation is slow and nitrogen retained in the char may be oxidized to nitric oxide in a second stage, it is advantageous to operate the first stage at high temperatures to devolatilize the coal nitrogen in the locally fuel rich environment. Although these strategies may be evident, the result of the present study provides a quantitative framework to guide the development of control strategy. For example, the kinetic data on the pyrolysis of coal can be used to estimate the temperature-time combinations required to devolatilize the nitrogen in the first stage of a staged combustor. In addition, the kinetic data on char oxidation may be used to size the second stage of the combustor. The staging, can of course, be achieved either by introduction of the combustion air at different positions in a furnace or by aerodynamic means.

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